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Defect Related Luminescence in Silicon Dioxide Network: A Review

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1. Introduction

The discovery of strong luminescence at room temperature from silicon cluster has attracted an enormous attention in recent years due to its potential applications in Si-based optoelectronic devices, especially blue and UV luminescence devices. Several studies have addressed the question of augmentation and stabilization of luminescence emission with different treatments, such as electron irradiation, thermal treatments and ion implantations. Even though observed visible light can be explained by the quantum confinement (QC) effect, many experimental results obey to the QC model supported surface state. Theoretically, the effects of quantum confinement on band gap of silicon indicate that it should be possible to obtain a blue light or shorter wavelength photons from the porous silicon if the silicon crystal size can be reduced to a certain value, e.g. to the diameter of 2-5 nm. However, it is rather difficult in practice to obtain a blue/white luminescence even when nanocrystals with diameters smaller than 2.0 nm are present. Some authors attributed this difficulty to the formation of surface Si-O bonds, which lead to mid-band gap trapped electrons and hole exciton states and thereby remove the dependency of the luminescence on cluster size. But in this case a luminescence emission was obtained in the red and yellow regions. It was found that some post-treatments such as anodic oxidation and oxidation in air could reduce the effective size of the Si nanocrystallites, thus causing a blue shift of the luminescence spectrum. If the red-yellow emission of the PS could be combined with a blue/green emission by modification of the PS surface such as oxidation or metal coating, it would be possible to obtain white light. This would mean an economical route to silicon based LEDs. Silicon dioxide, SiO_2 , is widely distributed in the environment, and is present in the form of sand on all beaches and deserts. It is the starting material for the production of silicate glasses and ceramics. It may occur in crystalline or amorphous form, and is found naturally in impure forms such as sandstone, silica sand or quartz. Its specific gravity and melting point depend on the crystalline structure. Silica is known to occur in many crystalline phases or modes (α -quartz, β -quartz, α -cristobalite, β -cristobalite, α -tridymite, β -tridymite, γ -tridymite, coesite, melanophlogopite, keatite, fassites, stishovite, chalcedon, agate, moganite, and others) besides some amorphous phases (opal, hyalite, sintered pearl, lechateierite, natural silica glass) [Fanderlik 1991]. Silicon dioxide is not only one of the most abundant materials on earth as mentioned, but also a critical material component of considerable technological importance. Today's modern electronics greatly depends on silicon dioxide for the manufacture of semiconductors and microelectronic devices, besides

it is the basic material of which the most of common communication optical fibers are presently made. In its pure amorphous form, it is drawn into fibers for use in optical communications. Its high melting temperature ($\approx 1700^\circ\text{C}$) and its chemical stability make it an excellent thermal and electrical insulator and hence the principal dielectric in silicon electronic technology, particularly in metal-oxide-semiconductor (MOS) devices [Nicollian and Brews 2002], where it is used as a gate oxide. High quality SiO_2 films are obtained by thermal oxidation of silicon; thermally oxidized SiO_2 forms smooth and low-defect interfaces with Si.

From a fundamental point of view, silicon dioxide is equally useful as a model amorphous material because of its chemical simplicity. It is not surprising that much research effort has been expended to understand the properties of this material. Despite hundreds of publications available, only in a few cases have an unequivocal identification of the atomic structure of the defects and an explanation of their production mechanisms been attained [Griscom 1977, Skuja 1998]. Most of the available information comes from theoretical models and other experimental investigations of naturally or synthetically prepared specimens, but many questions still remain unsolved. Accordingly, many of the optical features characterizing the as-grown material (that is the material prior to any treatment) are not attributable to a specific defect having a known structure. Also, the identification of the precursor of radiation-induced defects and the exact mechanism of their generation are still debated. As the number of device components on a chip continues to increase, where the performance and reliability of these devices are controlled by electrically active defects, the precise control of oxidation and its understanding on an atomic scale of silica has been a subject of great interest and importance in the modern Si technologies, especially those related to thin oxidize layers with high quality. It has been observed that irradiation, mechanical stress, temperature change and the presence of impurities can effect the formation of defects and/or the transformation of existing defects to other defects in SiO_2 [Mitchell and Denure 1973, Trukhin et al. 1998, Fitting et al. 2004]. Irradiation of SiO_2 induces various types of structural defects, which cause degradation in SiO_2 -based electronic and optical devices. Charge trapping at these defect sites degrades the current/voltage performance of metal-oxide semiconductor (MOS) devices, for example, and ultimately leads to device failure when such a device is exposed to high-energy radiation in space-based applications. Such and other problems are caused or at least initiated by the creation or transformation of luminescent point defects. Therefore a physical understanding of the structure and formation mechanisms of these defects is becoming increasingly important. But because of the nature of the chemical bond in silicon dioxide, a reliable guess of the detailed structure of particular luminescent defects has not been possible until now. A point defect embedded in a solid matrix (crystal or amorphous) is strongly interacting with its neighboring atoms. Then the study of the electronic states of the luminescent defects is a many-body particles system problem.

A half century of spectroscopy examinations of point defects in crystalline and glassy silica have led to identification and characterization of about a dozen intrinsic defect types (those constructed of silicon and/or oxygen atoms or ions) and around ten times as many defect varieties involving the presence of impurities. Luminescent defects in SiO_2 could be electrically charged or uncharged, diamagnetic or paramagnetic. Many such defects have been associated with optical absorption or emission bands, which may pose problems for long-path-length optical systems (fiber optics). Luminescent defects in amorphous silicon dioxide ($a\text{-SiO}_2$) have been defect investigated by numerous spectroscopic techniques,

including optical absorption spectroscopy (OA), electron spin resonance (ESR) or the often so-called electron paramagnetic resonance (EPR), photoluminescence spectroscopy (PL), photoluminescence excitation spectroscopy (PLE), cathodoluminescence spectroscopy (CL), infrared spectroscopy (IR), Raman spectroscopy and many more. All of these experimental approaches have yielded valuable insights, but have not given an explicit model for defect types in silica network. ESR spectra have afforded some detailed atomic-scale structure characterizations, especially of two fundamental classes of defects: a dangling electron on Si atom denoted by E' -center and the oxygen deficient center (ODC). These defects have been known in α -SiO₂ since 1956 [Weeks 1956].

2. Structures, defects and properties of silicon dioxide

2.1 Structure of pure silicon dioxide

The basic structural unit of vitreous SiO₂ and silicate glasses is the SiO₄ tetrahedron [Mozzi and Warren 1969, Bell and Dean 1972, Gerber and Himmel 1986]. A tetrahedron is a polyhedron composed of four triangular faces, three of which meet at each vertex. A regular tetrahedron is one in which the four triangles are regular, or "equilateral," and is one of the platonic solids (convex polyhedron). There are four oxygen atoms, one located at each apex of a regular tetrahedron and a single silicon atom is located at the center of the tetrahedron, Fig. 2.1. This silicon atom has a valence charge of 4 in sp^3 orbitals, meaning that it is looking to acquire four electrons through sharing with other atoms to complete its outermost energy shell, known as the valence shell. An oxygen atom has two electrons in its outermost shell that are available to bond with the silicon atom. If four oxygen atoms surround one silicon atom, where each oxygen atom offers one electron, then the silicon atom's outermost shell will be complete and stable. The resulting arrangement comprises a silicate molecule. One electron remains, allowing those oxygen atoms to search for another silicon atom to share an electron and form another tetrahedron. Tetrahedrons are linked together through oxygen bonds and the arrangement of these links between the basic tetrahedral units determines the classification of the silicate. When the tetrahedra are not linked together, as each exists in isolation, the material is classified as a Nesosilicate. If groups of two tetrahedra are linked together, the material is then classified as a Sorosilicate. If all of the tetrahedra link back onto each other to form a closed ring, then the material becomes a Cyclosilicate.

Fig. 2.1 Three-dimensional schematic of a pure fragment of the regular silica structure. The structure is defined by several parameters; the Si-O bond length (d), the tetrahedral angle (ϕ), the inter-tetrahedral bond angle (α), and the bond torsion angles (δ_1 , δ_2), [Henderson and Baker 2002].

The bonding in silicon dioxide is complex. The Si-O bond energy is very high (4.5 eV) compared to the Si-Si bond (2.3 eV) and has an approximately 50:50 ionic:covalent nature and lone-pair oxygen orbitals are present [Fanderlik 1991, Edwards et al. 2000]. The covalency favors tetrahedral coordination of Si by O and maintains the O-Si-O bond angle (ϕ) very close to the ideal tetrahedral angle of 109.5° . Some of the literature indicates that the Si-O bond length (d) in various modifications of silicates may vary in the range of 0.154 nm to 0.169 nm [Slater 1965, Weber and Cromer 1965], while the mean value specified for d is 0.162 ± 0.005 nm. In most cases one can treat the SiO_4 tetrahedra as rigid units, which can be linked together by their corners to form pairs, rings, chains, sheets, or frameworks. In this case the inter-tetrahedral Si-O-Si bond angle (α) can be defined. Measurements have been shown that the angle (α) varies with the different tetrahedra of the polyhedron, according to respective form of silicas (for vitreous SiO_2 from 120° to 180° and for quartz between 146° and 155°) [Fanderlik 1991, Nicholas et al. 1991].

Fig. 2.2 shows how the energy of a Si_2O_7 pair of tetrahedra varies as a function of Si-O bond length and the Si-O-Si bond angle [van Santen et al. 1991]. It is demonstrating that Si-O-Si bonds prefer to be linked rather than straight. However, the gently-sloping energy valley extending to 180° , which implies large variations in Si-O-Si bond angle (α) could occur in a structure with relatively slight energy penalty in order to accommodate changes in temperature, pressure, bulk composition, or local atomic environment. Silica does not produce any separate molecules ($\text{O}=\text{Si}=\text{O}$) because double bonds do not form. The parameters, such as the inter-tetrahedral bond angle (α) and the bond torsion angles (δ_1, δ_2), that define the way in which individual tetrahedra are linked together are highly variable [Mozzi and Warren 1969]. This variation in parameters distinguishes a glass from its corresponding crystalline analogue. To avoid the formation of a structural entity with an unsaturated electron cloud at the silicon atom in the case of a single bond, the $[\text{SiO}_4]^{4-}$ tetrahedra join to produce a polymer with various spatial arrangements. As a result of the alternative possibilities of structural arrangement, there exist a number of modifications of crystalline silica. In other words, the different types of silicate structure arise from the ways in which these tetrahedra are arranged. They may exist as separate unlinked entities, as linked finite arrays, as infinite one-dimensional chains, as infinite two-dimensional sheets or as infinite three-dimensional networks.

2.2 Intrinsic defects in silicon dioxide

The presence of defects in the silica matrix can dramatically change its structural, electrical, and optical properties. Many parameters, such as manufacturing processes, irradiation, mechanical stress, change of temperature, and the presence of impurities may cause the formation of defects and/or lead to the transformation of the existing defects to other types of defect. Commonly, defects can be grouped according to their structure and size as point defects, dislocations (linear defects), and plane defects [Stevens-Kalceff and Philips 1995, Kofstad 1988]. The following types of point defects can be considered as intrinsic or extrinsic. Intrinsic point defects involve atoms of the host matrix only, i.e. vacancies (the host atoms are missing, Schottky defects or Frenkel pairs) and self-interstitials (additional host atoms at an interstitial position). Extrinsic point defects involve atoms chemically different from the host crystal, such as those used for electrical doping. Defects in a perfect silica glass could include oxygen or silicon vacancies and their interstitials, Si-Si or O-O homobonds or under-coordinated silicons or oxygens.

Fig. 2.2 Total energy as a function of Si-O bond length and Si-O-Si bond angle. Contour lines in units of kJ/mol, [van Santen et al. 1991].

Due to the high Si-O bond energy (4.5 eV), the crystalline quartz is resistant to chemical weathering (it is only soluble in hydrofluoric acid and in hot alkalis) and to corrosion [Lamkin et al. 1992, Lide 2004]. It is hard (Mohs' hardness 7), brittle, and has a very high melting point at around 1710°C [Lide 2004]. Due to its wide energy band gap of about 9 eV, it is optically transparent and shows low electrical conductivity [Fan et al. 1998].

Generally, a homobond is electrostatically neutral although both Si-Si and O-O bonds may become positively charged by trapping holes. Irrespective of their electrical charges, defects can be divided into two classes: diamagnetic and paramagnetic. As a general rule, all stable paramagnetic defects have optical absorption bands associated with them, since they represent half-occupied energy transitions to the valence band and electron transitions to the conduction band are both possible. Diamagnetic defects may have absorption bands associated with electron transitions to the conduction band. The confirmed examples of diamagnetic defects in *a*-SiO₂ have electron absorption bands in the ultraviolet or vacuum ultraviolet spectral regions, implying that the uppermost filled levels of these states lie below the middle of the 9 eV band gap [Griscom 1977].

A variety of defect structures are known to exist in silica materials and were one of the major subjects of extensive experimental and theoretical studies [Stevens-Kalceff 2000, Song et al. 2001, Lu et al. 2002]. Many aspects regarding the nature of the defects and their correlated properties are still controversial and not yet completely understood. Quite a lot of defect types have been discussed in the literature and many reproduction models have been proposed for each one. In this part we will review the main defects in the silica network but whether any of these models is correct remains an open question of considerable interest.

2.2.1 *E'*-center

Probably the best known paramagnetic defect in all forms of SiO₂ is the *E'*-center which was first detected in late fifties using electron paramagnetic resonance (EPR) spectroscopy [Weeks 1956, Weeks and Nelson 1960, Griscom et al. 1974, Gobsch et al. 1978]. It is

associated with the 5.85 eV absorption band in quartz and silica glass and no associated emission band has been observed where its nonradiative mechanism has been reported by some authors [Pacchioni et al. 1998a , Kajihara K. et al. 2003]. From studies of the hyperfine structure in the EPR spectrum it is known that E' -center can comprise an unpaired electron in a dangling tetrahedral (sp^3) orbital of a single silicon atom which is bonded to just three oxygens in the glass network [Griscom 1979a, Isoya et al. 1981]. This generic E' -center is shown in Fig. 2.3, which is often denoted by $\equiv\text{Si}\bullet$, where the three parallel lines represent three oxygen separate bonds to one silicon atom and the dot denotes the unpaired electron.

Fig. 2.3 Generic E' -center. The large atom is silicon, the smaller ones are oxygens

Previous EPR studies on irradiated α - SiO_2 have demonstrated that there are several distinguishable variants of the E' -center in terms of their g values but in common all have the structure $\equiv\text{Si}\bullet$ [Griscom 1990a]. These E' -center variants are also distinguished by virtue of different annealing kinetics depending on both the character of the irradiation and the water contents in dry or wet oxidized SiO_2 , as shown in Fig. 2.4 [Griscom et al. 1983, Griscom 1984, Griscom 1985].

Four main types of E' -centers, labeled E'_α , E'_β , E'_γ and E'_s have been identified in vitreous silica depending on their spectroscopic signatures [Skuja 1998]. Several models have been suggested based on different precursors for each of these defects where some of these types are associated with hydrogen atoms. Optically stimulated electron emission technique (OSEE) shows that each one of these types of E' -centers has a distinguishable absorption band in the range of 5.7 eV [Zatsepin et al. 2000], see Fig. 2.5.

Fig. 2.4 Normalized isochronal anneal curves for radiation-induced defect centers (E' , NBOHC and peroxy radical) in high-purity silica (low-OH silica: <5 ppm OH and high-OH silica: 1200 ppm OH), [Griscom 1984].

Fig. 2.5 OSEE spectra of glassy SiO₂ irradiated by Fe⁺ ions of two different energies, 30 and 100 keV, the absorption bands of E'_β , E'_γ and E'_s -centers are detected, besides a very weak absorption band associated with oxygen deficient centers (ODC), [Zatsepin et al. 2000].

It was inferred that the E'_α variant in silica initially observed by Griscom [Griscom 1984], is a defect which tends to anneal in times on the order of minutes up to hours above 100 K. It was suggested that this center is created by a radiolytic process which moves an oxygen atom from an undisturbed network site $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ into a neighboring position which must be chemically bonded, since insufficient energy can be transferred from an X-ray generated compton electron to result in a net breakage of bonds [Uchino et al. 2001]. Fig. 2.6 illustrates one of the conceivable ways in which such a process could come about. The oxygen-oxygen (peroxyl $\equiv\text{Si}-\text{O}-\text{O}$) bond suggested to be formed in Fig. 2.6 should be a relatively stable entity according to recent theoretical calculations [Griscom 1979a]. Still, less exotic mechanisms for E'_α production, not inconsistent with the data, might be the momentary rupture of strained oxygen bonds $\equiv\text{Si}\cdots\text{O}-\text{Si}\equiv$. Here $\bullet\text{O}-\text{Si}\equiv$ is the notation for the non-bridging oxygen hole center (NBOHC), and is in fact seen by electron spin resonance (ESP) in X-ray irradiated silicas in numbers comparable to the E'_α -center.

Fig. 2.6 Schematic models for the E'_α -center in pure α -SiO₂, the arrow denotes the unpaired spin and dashed balloons represent their orbital.

E'_β in silica network (E'_2 in quartz) features a proton trapped in the oxygen vacancy and the silicon atom containing the unpaired spin relaxed outwards [Griscom 1991, Weeks 1963], i.e.

the interaction of the unpaired spin associated with a long-bond silicon with the hydrogen atom is weak enough to not saturate each other. Two possible formation reactions of E'_β are shown in Fig. 2.7.

Fig. 2.7 Schematic models for the E'_β -center in pure α -SiO₂. The arrow denotes the unpaired spin and dashed balloons represent their orbital. The E'_β -center is considered to be the closest analog for E'_2 -center in quartz.

E'_γ -center is the closest analog of the E'_1 -center in α -quartz [Griscom 1980, Boero et al. 1997]. According to current theoretical calculations [Feigl et al. 1974, Yip and Fowler 1975, Mysovsky et al. 2004], E'_γ is suggested to consist of a positively charged single oxygen vacancy composed of a nearly planar $\equiv\text{Si}^+$ unit and a singly occupied dangling bond $\equiv\text{Si}\bullet$, namely, $\equiv\text{Si}^+ \bullet\text{Si}\equiv$ [Uchino et al. 2000b, Agnello et al. 2002]. An unrelaxed oxygen monovacancy ($\equiv\text{Si} \cdots \text{Si} \equiv$) or an unperturbed SiO₂ fragment ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) is assumed to be the precursor of this defect as shown in Fig. 2.8. There is no indication that hydrogen is involved in this defect [Feigl et al. 1974]. E'_γ is stable for years at room temperature [Griscom 1984].

Fig. 2.8 Schematic models for the E'_γ -center in pure α -SiO₂. The arrow denotes the unpaired spin and dashed balloons represent their orbital. The E'_γ -center is considered to be the closest analog for E'_1 -center in quartz.

Relaxing of the Si atom with the unpaired spin towards oxygen vacancy results in the E'_4 -center. It is in fact the most reliably characterized of these defects depending on the experimental and theoretical analysis [Isoya et al. 1981]. E'_4 -center consists of a hydrogen substituting for an oxygen atom in α -quartz [Mysovsky et al. 2004]. This center, Fig. 2.9, is observed in crystalline silicon dioxide (α -quartz) but there is no evidence of existence of E'_4 -center in silica glass [Griscom and Friebele 1986]. Some other authors [Rudra et al. 1985, Majid and Miyagawa 1993, Snyder and Fowler 1993] suggested that the E'_2 and E'_4 are in fact the same defect, but with long-bond silicon relaxed through the plane of its three oxygen neighbors such that the unpaired spin points away from the vacancy. But this configuration is predicted to be slightly lower in energy than the E'_4 configuration. In surface center studies, several variants of surface E' -centers were found [Bobyshev and Radtsig 1988]. Two of them are depicted in Fig. 2.10, $E'_s(1)$ which seems like the normal E' -center but with a constant isotropic hyperfine splitting, and the second is $E'_s(2)$ which has a dangling silicon bond with a neighboring hydroxyl (OH) group [Skujia 1998].

Fig. 2.9 Schematic model for E'_4 -center in crystalline SiO_2 . The arrow denotes the unpaired spin which interacts with a hydrogen atom to relax the oxygen vacancy by forming Si-Si bond.

Fig. 2.10 Schematic models for surface E' -center (E'_s) in pure $a\text{-SiO}_2$. The arrow denotes the unpaired spin and dashed balloons present their orbital. Hydrogen saturates the dangling oxygen bond

2.2.2 Oxygen-deficiency center (ODC)

It should be mentioned first that all E' -center types are also considered as oxygen deficiency centers but in this subsection a review of a different (non-paramagnetic) kind of oxygen deficiency center will be given. This defect center is entitled simply by a neutral oxygen vacancy which is often denoted ODC and indicated generally as $\equiv\text{Si}-\text{Si}\equiv$.

Fig. 2.11 Schematic illustration of the transformation between ODC(I) and ODC(II) visualizing two possible models for the ODC(II), the unrelaxed oxygen vacancy and the twofold coordinated silicon.

It is diamagnetic and can be directly investigated by photoluminescence (PL) or cathodoluminescence (CL) spectroscopy. The literature mostly describes two models for the ODCs: neutral oxygen vacancy ODC(I) and the twofold coordinated silicon ODC(II) denoted as $\equiv\text{Si}\bullet\bullet$. The ODC(I) represents one of the essential defects in all silicon dioxide modifications in a form of simple oxygen vacancies; here two Si atoms could relax and make a silicon silicon bonding (relaxed oxygen vacancy $\equiv\text{Si}-\text{Si}\equiv$) or stay in unstable interaction condition and form an unrelaxed oxygen vacancy ($\equiv\text{Si}\cdots\text{Si}\equiv$) which each one of them could be a precursor for the other under some undeclared circumstances, see Fig. 2.11, and both are considered as a key role in many defect-type generations and transformations in the silica matrix, as shown in Figs. 2.7 and 2.8. The 7.6 eV absorption band in irradiated and as grown $a\text{-SiO}_2$ has been ascribed to the neutral oxygen vacancy ODC(I) [Imai et. al 1988,

Hosono et al. 1991]. The ODC(I) can also be converted to $\equiv\text{Si-H}$ groups in thermal reaction with hydrogen molecules according to the visualized reaction shown in Fig. 2.12.

Fig. 2.12 Schematic illustration of the ODC(I) conversion to silanol groups in thermal reaction with hydrogen molecules.

In addition, two photoluminescence (PL) bands, 4.4 eV (decay constant $\tau=4$ ns) and 2.7 eV (decay constant $\tau=10.4$ ms) have been observed under excitation of the 5 eV, 6.9 eV or 7.6 eV bands, indicating the interaction of ODC(II) with ODC(I) [Nishikawa et al. 1994, Seol et al. 1996]. Based on their lifetimes, the 4.4 eV and 2.7 eV bands have been ascribed to singlet-singlet ($S_1 \rightarrow S_0$) and triplet-singlet ($T_1 \rightarrow S_0$) transitions at the site of oxygen-deficient type defects, respectively [Skuja 1998]. The interconversion between the ODC(I) and ODC(II) in an energy diagram is given in Fig. 2.13. The origin of ODC(II) associated with the optical absorption band at ~ 5 eV is one of the most controversial issues in the defect research field of a-SiO₂ [Skuja et al. 1984, Griscom 1991, Skuja 1992a, Skuja 1998]. The first model hypothesis suggested for ODC(II) was a neutral diamagnetic oxygen vacancy [Arnold 1973], later two other models have been proposed for ODC(II): twofold coordinated silicon [Skuja et al. 1984, Skuja 1992a] and the unrelaxed oxygen vacancy [Imai et al. 1988] as shown in Fig. 2.11. The oxygen vacancy model was further supported by the finding that two-photon photobleaching of SiODC(II) by KrF laser ($\hbar\omega=5$ eV) generates E' -centers [Imai et al. 1988]. But the origin of the ODC(II) is still a matter of controversy.

Fig. 2.13 Diagram of the energy levels proposed for the optical transitions at the site of two oxygen-deficient centers: ODC(I) and ODC(II). Transformation between the two states is assumed by the excitation at 7.6 eV. Solid and dotted arrows represent radiative and non-radiative electronic transitions, respectively. ΔE_{act} is the thermal activation energy for singlet-triplet conversion, τ are the radiative decay times, [Skuja 1998 and Nishikawa 2001].

2.2.3 The non-bridging oxygen hole center (NBOHC)

This center can be visualized as the oxygen part of a broken bond (Figs. 2.6 and 2.15). It is electrically neutral and paramagnetic and represents the simplest elementary oxygen-related intrinsic defect in silica. It is well characterized both by EPR and by optical spectroscopies like photoluminescence (PL) and cathodeluminescence (CL). The main optical characteristics of NBOHC are shown in Fig. 2.14, it has an absorption band at 4.8 eV with FWHM=1.07 eV, oscillator strength $f=0.05$; an asymmetric absorption band at 1.97 eV, FWHM=0.17 eV, $f=1.5\times10^{-4}$; a photoluminescence band excited in these two absorption bands, at 1.91 eV , FWHM=0.17 eV, decay constant around 20 μ s. Out of these three characteristics, the most unique fingerprint of this center is the 1.9 eV luminescent band in the red region of the visible light spectra. It has been postulated that the NBOHC arises when hydrogen atoms are liberated radiolytically from one member of a pair of OH groups in wet silica (high OH group) according to Fig.2.15 [Stapelbrok et al. 1979].

Fig. 2.14 Optical absorption and luminescence spectra of γ -irradiated wet silica illustrating the main optical properties of NBOHC: the absorption/excitation bands at 4.8 eV and 1.97 eV, and the photoluminescence band at 1.9 eV, [Pacchioni et al. 2000].

Fig. 2.15 A model of atomic structure of the non-bridging oxygen hole center (NBOHC) showing the possible generating processes of NBOHC in wet silica.

Fig. 2.16 Energy band diagram of different NBOHC energy states, [Munekuni et al. 1990].

However this reaction is not the only way of creating NBOHC. Oxygen dangling bonds may be created as well in wet and in dry silica (negligible amounts of OH groups) by rupturing of the strained Si–O bonds ($\equiv\text{Si}\cdots\text{O}-\text{Si}\equiv$) in the silica network (Fig. 2.6). Particularly there are no spectroscopic distinctions which have been established between the centers formed by these two precursors, but on the other hand some authors [Munekuni et al. 1990] proposed some differences in their emission energies, see Fig. 2.16.

If softer irradiation (X-ray) was used, the centers were created only in groups of Si–O–R (R: alkali ion). This behavior provides evidence that the centers are created in reactions similar to that visualized in Fig. 2.15, and they were attributed to NBOHC [Skuja 1994a, Skuja et al. 2006]. On silica surfaces, the same red luminescence band can be created by adding O atoms to surface E' -centers [Streletsky et al. 1982]. Another generic oxygen hole center is the self-trapped hole (STH), which exists in two different variants. STH_1 comprises a hole trapped on a normal bridging oxygen in the network ($\equiv\text{Si}-\text{O}^\bullet-\text{Si}\equiv$), while the STH_2 is suggested to consist of a hole delocalized over two bridging oxygens [Griscom 1991, Griscom 2000].

2.2.4 Peroxy bridge (POL)

In oxygen-excess silica, some of the excess oxygen is expected to form "wrong" oxygen-oxygen bonds, called peroxy bridges or peroxy linkages ($\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$). Calculations of atomic oxygen diffusion in SiO_2 suggested that POL structure is the lowest energy configuration for an oxygen interstitial [O'Reilly and Robertson 1983]. However, a definitive spectroscopic confirmation of their presence in silica is still absent. The experimental evidence is only indirect, but it is thought to be responsible for the exclusive (without the accompanying Si–H groups) generation of Si–OH groups during H_2 treatment of oxygen rich silica [Imai et al. 1987], as shown in Fig. 2.17. This reaction is accompanied by an increase of VUV optical absorption for $h\nu > 7$ eV indicating that the POL could possibly absorb in this region. POL was initially suggested to be the main precursor of peroxy radical defects, Fig. 2.18, as we will show in the following subsection [Friebele et al. 1979]. The calculation put the energy of the POL absorption band at around 6.4–6.8 eV with a small oscillator strength, $f=2\times 10^{-4}$ [Pacchioni and Ierano 1998b], such absorption would be hard to detect against the background of other bands in vacuum UV.

2.2.5 Peroxy radical (POR)

The Peroxy radical (POR) in silica is a paramagnetic defect with a hole delocalized over anti-bonding π -type orbitals of the O–O bond in the structure illustrated in Figs. 2.17 and 2.18. EPR spectroscopy shows that the POR is the best characterized oxygen excess defect in silica

Fig. 2.17 Models presenting the suggested atomic structure of a peroxy bridge (POL) and its role in producing other possible defects in silica matrix.

Fig. 2.18 Models presenting some possible generation modes for the peroxy radical (POR) structure in the silica matrix.

[Griscom 1991, Friebele et al. 1979]. However, the optical properties of POR in bulk silica are not accurately known. Good correlations between the isochronal annealing curves of EPR signals of POR and of the optical absorption band at 7.7 eV were reported in γ -irradiated dry silica [Stapelbroek et al. 1979]. The optical absorption spectrum observed for peroxy radicals on the surface of SiO₂ by the diffuse reflectance technique in the region around 5.4 eV with FWHM 1.3 eV and oscillator strength $f \approx 0.067$ was calculated [Bobyshev and Radtsig 1988].

2.2.6 The self-trapped exciton (STE)

The electronic excitation of solids produces mainly electrons, holes and excitons. Transient (short living) defects can be created through the combination of the electronic excitation energy of electron-hole pairs and electron-phonon interaction. The conversion of excitation to defects is initiated by self-trapping of excitons, by the trapping of electrons by self-trapped holes or by the consecutive trapping of an electron and hole by a defect. These transient defects can produce either radiative or non-radiative electronic transition, while non-luminescent transient defects disappear by recombination of defect pairs. Self-trapping is a widespread phenomenon in insulators [Hayes and Stoneham 1985, Song and Williams 1993].

The existence of the self-trapped excitons in crystalline SiO₂ is supported by experimental measurements of the optically detected magnetic resonance and transient volume change [Itoh et al. 1988]. The luminescence bands between 2 and 3 eV in the silica spectrum have been ascribed to the STE. Some authors suggested that the STE is the source of the characteristic blue luminescence in crystalline SiO₂, but it has been observed that this luminescence band is removed in quartz by intense electron irradiation (15 keV) at room temperature due to the electron hole recombination as shown in Fig. 2.19 [Griscom 1979b, Trukhin 1978, Trukhin 1980, Barfels 2001]. Almost the same luminescence band can be detected in the emission spectra of amorphous SiO₂ but with much lower intensities than the

other characteristic bands. STE perturbed by small distortions due to a structural defect give emissions in the same energy range. For example, Ge implanted quartz exhibits a luminescence band at 2.5 eV close to 2.8 eV in non-implanted quartz [Hayes and Jenkin 1988]. The excitation spectra for STE luminescence in α -quartz show a peak at 8.7 eV, which is ascribed to the first exciton peak. The absorption edge has been determined as 9.3 eV [Itoh et al. 1989], so the exciton binding energy is about 0.6 eV for α -quartz [Bosio and Czaja 1993]. The large energy difference between the band edge absorption (about 9 eV) and luminescence (2.8 eV) points to strong electron-photon coupling. The optical absorption spectra and the excitation spectra for fused silica are similar to those of α -quartz but exhibit modifications due to the amorphous structure [Trukhin 1992].

Fig. 2.19 CL-spectra of some crystalline SiO₂ (Quartz and Stishovite) at 290 K and 80 K, [Barfels 2001].

Meanwhile, several models have been proposed implying to clarify the STE. One of the first models considering that an oxygen atom will removed to a peroxy bridge position [Griscom 1979a, Griscom 1979b] and other models are based on the proposition that a threefold coordinated silicon explains the transient absorption at 5.2 eV (E' -center) [Trukhin 1992, Trukhin 1994], see Fig.2.20. All of these suggested models are based on the idea that the silicon-oxygen bond (Si-O) gets ruptured and forms an oxygen-oxygen bond (–O–O–) based on the fact that different local structures of the SiO₂ network provide different distances for oxygen-oxygen bonding. Each oxygen atom bonded to two silicon atoms by two types of Si-O bond, one by long bond ≈ 1.612 Å and another by short bond ≈ 1.607 Å, as shown in Fig. 2.20 by dashed and solid bond connections [Hayes et al. 1984, Trukhin 1994]. These models explain different STE luminescence properties of different structures.

Fig. 2.20 Models of self-trapped exciton (STE) showing a creation of oxygen vacancy, E' -center and peroxy bridge due to the decay of a STE associated with an excited Si–O bond in crystalline SiO₂.

2.2.7 Interstitial oxygen

Mostly all variants of manufactured high-purity dry SiO_2 contain natural interstitial oxygen atoms and an additional amount can be generated by ejecting oxygen atoms from their normal sites in the SiO_2 network during the irradiation. Another important point that has to be considered is the molecular oxygen. Principally O_2 molecules can be formed in irradiation processes from the already present oxygen atoms [Morimoto et al. 1992]. The first spectroscopic observation of O_2 molecules in silica was performed by Raman spectroscopy in optical fibers [Carvalho et al. 1985]. O_2 was detected by O–O stretching vibration at wavenumber 1549 cm^{-1} . Using this method the O_2 molecule concentration is found to be in the range of 10^{14} – 10^{18} molecules per cm^3 in dry silicon dioxide [Skuja et al. 1998a].

In gas phase, oxygen molecules (O_2) dissolved to two atomic oxygen (2O) for $h\nu > 5.1\text{ eV}$ ($\lambda < 242\text{ nm}$); the same can be expected to occur in silica glass following the photolytic reaction shown in Fig. 2.21. The atomic oxygens appearing as a result of this reaction might be expected to be relatively mobile in silica even at room temperature; then they interact with other oxygen molecules to form ozone (O_3) just as it occurs in the earth's atmosphere [Baulch et al. 1980, Finlayson-Pitts and Pitts 1986]. There are indications that the atomic oxygen becomes mobile at around $400\text{ }^\circ\text{C}$ as detected by formation of the interstitial oxygen molecules at this temperature [Skuja et al. 2002, Kajihara et al. 2004]. Depending on the quantum yield for the gas-phase reaction of ozone dissociation, it is believed that O_3 molecules are responsible for both the 4.8 eV absorption and 1.9 eV luminescence in certain oxygen-rich silicas [Awazu and Kawazoe 1990, Griscom 1991, Skuja et al. 1995], which usually are attributed to the NBOHC by many authors [Kajihara et al. 2001, Cannas and Gelardi 2004, Bakos et al. 2004b]. The 1.9 eV luminescence band shifts between 1.8 and 2 eV depending on the excitation wavelength within the 2 eV absorption band [Skuja et al. 1995]. Other bands of possibly related origin have been observed in the 2.0 – 2.5 eV regions [Munekuni et al. 1990, Skuja 1994a]. O_2^- and O_3^- can be other candidates for the 1.8 eV band but the only truly unanimously agreed point is that the 1.8 eV luminescence band is related to excess oxygen in silica [Skuja et al. 1995].

Although the amount of interstitial O , O_2 and O_3 can be negligible in comparison with the whole oxygen content in a silica network, the presence of these interstitial atoms or fragments has to be considered when analyzing a large amount of accumulated defects in the silica matrix.

Fig. 2.21 Main interstitial atomic and molecular oxygen as well as ozone model in SiO_2 .

2.2.8 Hydrogen-related defects and the state of water in SiO_2

Hydrogen in the form of steam has been used intentionally during thermal oxidation to increase oxidation rates. Very often it is also incorporated unintentionally into SiO_2 layers. Hydrogen is proposed to passivate the silicon or oxygen dangling bonds in SiO_2 network [Cartier et al. 1993, Fair 1997]. This passivation also decreases the number of non-bridging

oxygen which in turn reduces the viscosity of the silica layers substantially [Rafferty 1989]. Some authors considered hydrogen to be an intrinsic defect since it is commonly found in silicon dioxide. Hydrogen and water are ubiquitous impurities in SiO_2 . The energy levels of silanol ($\equiv\text{Si}-\text{O}-\text{H}$) and hydride ($\equiv\text{Si}-\text{H}$) groups have been calculated by tight-binding calculation [Robertson 1988]. The hydride groups seem to produce a filled s state just below the valence band (VB) and an empty σ^* state in the gap just below the conduction band (CB). This group is probably both an electron and a hole trap.

Hydride groups are expected in thermally grown silica, particularly near the interface due to the interaction of interstitial H_2 molecules with $\text{Si}-\text{O}-\text{Si}$ bridges. The H_2 is a byproduct of the fast oxidation of Si by any ambient water.

Fig. 2.22 A model of the structural state of water in SiO_2 network and its transformation to silanol groups, [Brunner et al. 1961, Bakos et al. 2004a].

Fig. 2.23 A model of the structural state of water in SiO_2 lattice and its formation, [Nuttall and Weil 1980, McLaren et al. 1983].

It is proposed that water can be incorporated into the SiO_2 lattice according to the reaction illustrated in Fig. 2.22 [Brunner et al. 1961, Bakos et al. 2004a]. This is a preferred stress-induced mechanism and referred to "as hydrolytic weakening" [Griggs and Blacic 1965, Griggs 1967]. Calculations of total energy indicate that this reaction which uses an energy of ~ 0.1 eV is spontaneous for a $\text{Si}-\text{O}$ bond stretched beyond 4% of its normal bond length [Heggie 1992]. It has also been suggested that the solubility of water in the quartz lattice depends on the aluminum content [Kronenberg et al. 1986].

Another possible configuration shown in Fig. 2.23, assumes that hydrogen is incorporated in the quartz structure by means of $(4\text{H})\text{Si}$ defects where 4H^+ substitutes for Si^{4+} [Nuttall and Weil 1980, McLaren et al. 1983].

3. Fundamental of cathodoluminescence

3.1 Electron beam interaction with matter

When an electron hits a solid surface, it penetrates into the microstructure of the solid and interacts with its atoms. The resulting effects allow the extraction of analytical information

Fig. 3.1 Schematic representation of processes resulting from electron bombardment (modified after Reimer 1998). Note that the emissions come from different depths, e.g. CL and X-rays are emitted from deeper section levels than the secondary electrons.

on various properties of the material. The elementary interaction process involves collision of the electron with an atom, either with the positive atomic nucleus or with the electrons. Since the colliding particles are charged, the interaction is governed essentially by electrostatic Coulomb force. In an electron-nucleus collision, the atomic nucleus hardly changes its position since it is much heavier than the electron. The electron is therefore deflected at the nucleus without significant energy loss (elastic scattering). If the electron collides with the electrons of the atomic shells, then energy is transferred due to the equal masses of the colliding particles (inelastic interaction). Both scattering processes operate simultaneously side by side and provide a wide variety of useful signals. As a consequence of these different scattering events, an electron probe which originally was sharply focused in vacuum spreads over a greater volume after penetrating the solid. The shape and size of this scattering volume depends upon the material as well as the energy and angle of incidence of the probe electrons [Reimer 1998].

The elastic interactions between electrons and atoms or between electrons and the crystal lattice gives rise to a number of effects; the emission of secondary electrons (SE), backscattering of electrons (BE), Auger electrons (AE), characteristic X-ray (EDX) and cathodoluminescence emission (CL) but mainly most of the electron beam's energy will be absorbed (sample current) and converted into heat (phonons) [Ozawa 1990]. AEs and more generally SEs can only escape from the first few nanometers of the surface. This means that these signals originate from the top of the interaction volume, the lateral size of which is determined by the electron probe size which in turn defines the spatial resolution in AES and SEM. Backscattered electrons are higher in energy and can escape from deeper areas below the surface where the interaction volume is wider laterally, this results in a degraded image resolution for backscattered electron imaging in the SEM relative to that of secondary electron imaging [Reimer 1998]. Analyzing these signals may provide valuable information about the surface and atomic structure of the investigated substance. Two of these signals

Fig. 3.2 Energy band diagram of one-dimensional lattice, [Yacobi and Holt 1990].

were among our main interest in this study, CL for luminescence defects investigation and EDX used for the atomic element component analysis. Fig. 3.1 illustrates schematically these effects and their major common applications.

The term cathodoluminescence (CL) designates the luminescence induced by energetic electron bombardment. Cathodoluminescence is excited from the region near the surface of the specimen and up to deeper than X-rays excitation volume, see Fig. 3.1. Therefore, the energy of the incident electron beam can be rather low (1-5 keV) to excite significant cathodoluminescence signals of use for the various applications. The CL signal is formed by detecting photons of the ultraviolet (UV), visible and near-infrared (IR) regions of the spectrum. These photons are emitted as the result of electronic transitions between the conduction and valence bands in semiconductors, and transitions between energy levels lying in the band gap of materials with wide band gap (insulators), Fig. 3.2. Many useful signals in these cases are due to transitions that involve impurities and a variety of defects.

X-ray spectrometry is based on the emission of X-rays from the atoms of a solid when struck by particles or waves of sufficiently high energy (electron beam in our case), followed by the relaxation of the atoms to the ground state after ionization. The X-ray spectrum produced by electron excitation consists of two parts, a continuous spectrum of deceleration radiation, known as "bremsstrahlung", and a line spectrum of the characteristic radiation. Characteristic X-rays will only be excited in the volume in which the electron energy exceeds the ionization energy of the inner shell involved. The general concept of X-ray emission-region and emission-process are shown in Figs. 3.1 and 3.2. The electron beam energy is typically in the range 10-20 keV and the energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 1-4 μm in depth, thus EDX is not a surface science technique, but it is a method used for providing sample composition information besides charging properties of insulators. Both CL and EDX techniques are commonly used in combination with a scanning electron microscope (SEM).

3.2 Process of luminescence excitation

Luminescence is produced by electron transitions between different energy levels. It may be produced by a band-band transition, transitions from band to localized state, or even between two localized states in a defect molecule, see Figs. 3.3 and 3.4. Luminescence is considered to form mainly in three steps. First, absorption of the excitation energy and stimulation of the atoms into an excited state, then transformation and transfer of the

Fig. 3.3 Mechanisms of cathodoluminescence due to recombination processes in semiconductors or insulators: (a) recombination by direct band-to-band transition leads to intrinsic cathodoluminescence ; (b-e) recombination via localized states in the forbidden gap results in extrinsic cathodoluminescence; (f) excitation and recombination within the defect energy levels. E_a =acceptor level, E_d =donor level, modified after Krbetschek et al. 1997.

excitation energy, and finally emission of light and relaxation to a non-excited state [Yacobi and Holt 1990]. The first two steps mainly depend on the mode of excitation, whereas the third step depends on the character of specific luminescence centers.

In crystals, complex interaction between atoms leads to the broadening of the energy levels into bands. In insulators like silica, a broad gap, called the forbidden gap, exists between the valence band and the conduction band. A precondition for cathodoluminescence is the existence of activators (impurity ions, lattice defects), which cause and occupy discrete energy levels in this forbidden zone. Luminescence centers can be differentiated by their energy position within the forbidden gap and divided into electron traps near the conduction band (donor level) and recombination sites in the vicinity of the valence band (acceptor level).

CL involves electron radiation induced excitation of an electron from the ground state to an excited state. Recombination of an electron from the conduction band with a hole in the valence band is possible in variety of ways: it may take place by a band-to-band transition or step by step via localized energy states within the forbidden gap. In a band-to-band transition shown in Fig. 3.3a, light is emitted with a photon energy $h\nu = E_g = E_c - E_v$; this type of CL is called intrinsic luminescence. Intrinsic CL is only likely to occur in semiconductors (GaAs and ZnS) in which recombination can take place directly, i.e without changes in momentum. In indirect semiconductors (Si, Ge, and GaP) the special band structure requires a photon to take part in the recombination process so that momentum is conserved.

The extrinsic CL is a recombination that takes place via localized energy states within the forbidden gap. Excitation results in the trapping of an electron or in the recombination with a luminescent or a non-luminescent center (Fig. 3.3b). In the case of a luminescent transition, a photon is emitted. If the atom or the ion is placed in a crystal lattice, non-luminescent transitions are possible due to absorption or emission of lattice vibrations. A trapped

electron can be excited again, transits into the conduction band and may recombine with an activator element level resulting in emission of a photon (Fig. 3.3c), or a trapped electron may relax to the valence band and emit a photon (Fig. 3.7d). In the case of a small energy difference between electron trap and activator level, a direct luminescent transition of the electron to the recombination centre is possible (Fig. 3.3e). A More complex process is the excitation of several energy states lying deeper inside the forbidden gap and the subsequent relaxation and luminescence emission of a single activator is also possible (Fig. 3.3f). Such states can be due to point defects (impurities or lattice defects) and act as traps for electrons or holes. The variety of possible transitions and the thermally induced broadening of the energy states make the CL spectra very difficult to interpret.

Fig. 3.4 Possible processes of excitation of a luminescence center explained in depending on configuration coordinate diagram assuming (a) radiative transition , (b) non-radiative transition , and (c) thermally assisted excitation into the conduction band, [Krbetschek et al. 1997].

The process of excitation and emission of an individual luminescence center can be described using a configuration coordinate diagram. It shows the potential energy curve of the absorbing center as a function of the relative distance (r) of the nucleus to the equilibrium position (electron in the ground state). Fig. 3.4 shows excitation of a defect atom/molecule from the ground state (Q_i) to excited state (Q_f) combined with radiative (Fig. 3.4a) and nonradiative (Fig. 3.4b) relaxation. As a particular case of excitation, thermally assisted excitation (Fig. 3.4c) into the conduction band and the relationship between the configurational coordinate and the band model are also shown.

In optical absorption (E_a) the center is promoted from the ground state to a higher vibration level of the excited state. After relaxation (R) to the zero vibration level of the excited state the electron returns with luminescence emission (E_e) or via a nonradiative transition with the emission of photons (ρ) and relaxes to the zero vibrational level (R_o). Since the electron transitions are faster than lattice relaxation, the absorption occurs adiabatically as a vertical transition (the Frank-Condon principle). The energy difference between absorption and emission is called Stokes shift. A special case of the excitation is thermally assisted ionization (Fig. 3.4c). After excitation to a higher energy level, the electron can escape to the conduction band (CB) by phonon absorption and recombine with other activators. This process may form the basis of infrared stimulated luminescence in feldspars [Hütt et al.

1988]. More complex processes may result from charge transfer. The electron is excited by high energy excitation into the charge transfer band and stored in a trap. After a second excitation with lower energy (e.g. thermal, infrared radiation) the electron escapes from the trap to an activator by a radiative or nonradiative transition. The life time τ of the trapped state depends on the depth (energy level) of the trap and the temperature, and can be determined using the Boltzmann relation $\tau = s^{-1} \exp(E/K_B T)$, where s is frequency factor, τ the absolute temperature and E the activation energy, i.e. the energetic depth of the trap.

3.3 Luminescence emission bands in silicon dioxide

The real structure of silica materials significantly influences their luminescence behavior. Moreover, defect contents and implanted elements dramatically changes the cathodoluminescence (CL) properties of silicas. The luminescence of silica is generally weak at room temperature, but it is highly variable depending on the specific conditions of silica formation. Crystalline SiO_2 modifications and amorphous silica show similar main luminescence bands. This is due to the fact that short-range order defects in silicate structure are determined mainly by silicon-silicon and silicon-oxygen interaction rather than by interactions between oxygen atoms [Berry and Vaughan 1985]. Since a strict correlation between the intensities of CL bands and concentrations of specific defects or trace elements does not exist, the interpretation of the origin of luminescence of silica materials is difficult. Furthermore, the band positions of the luminescence emissions can vary depending on the particular SiO_2 structure and the experimental conditions. The CL spectra of silica consist mainly of several emission bands in the blue up to the red spectral region. Investigation of natural and synthetic silica specimens show various emission bands which are ascribed to different intrinsic and extrinsic defects. The CL spectra of silica materials are generally consist of some different broad emission bands (defect's optical bands) instead of sharp spectral lines. Overlapped bands are commonly expected too, and it seems to be difficult to resolve these bands to their real components. Two reasons for the broadening of these transitions have been suggested: the first is due to the different static local environments (inhomogeneities) of defects in disordered glass called inhomogeneous broadening, and the second is due to the coupling of electronic transition to phonons called homogeneous broadening. The homogeneous broadening is the same for all related defect sites throughout the sample and occurs even for defects in otherwise ideal crystal. The main contribution to the defect's optical bands broadening (FWHM) in amorphous SiO_2 which is our main interest in this study, is usually from homogeneous broadening (0.2-1 eV) while the magnitude of inhomogeneous broadening is of the order 0.1 eV [Skuja 2000]. Table 3.1 summarizes the main PL and CL emission bands previously reported for $\alpha\text{-SiO}_2$ and $a\text{-SiO}_2$ and their proposed associations. Further on, cathodoluminescence can be divided into two categories: intrinsic CL, which is characteristic of the host lattice, and extrinsic CL which results from impurities. Larger defects such as dislocations and clusters may also have an effect on the CL signal. Intrinsic luminescence is enhanced by non-stoichiometry (vacancies), structural imperfections (poor ordering, radiation damage, shock damage), and impurities (non-activators), which distort the crystal lattice. The CL properties are mostly the result of luminescence-activating ions such as transition metals, rare-earth elements or actinides. Changes of the crystal field properties i.e., field strength, site symmetry, and coordination number, cause differences in the magnitude of the energy levels of the activator elements and also the splitting of closely spaced levels.

Table 3.1 (a): Reported CL and PL luminiscent bands in amorphous silicon dioxide (*a*-SiO₂) and crystalline quartz (*α*-SiO₂) and their proposed associations in IR-Green region.

wave length (nm)	energy (eV)	CL, PL emission band (eV)	Specimen	Association	References
1240	1.00	0.97	<i>a</i> -SiO ₂ & <i>α</i> -SiO ₂	O ₂ , O ₂ ⁻	Skuja et al. 1998b, Stevens-Kalceff 2000
1181	1.05				
1127	1.10				
1078	1.15				
1033	1.20				
992	1.25	1.3 - 1.75	C & Si doped <i>a</i> -SiO ₂ <i>a</i> -SiO ₂ and <i>α</i> -SiO ₂	Si & C nanocluster Si-nanocluster	Chae et al 1999, Rebohle et al. 2001a Takagahara & Takeda 1992, Shimizu-Zunger & Wang 1996, Kim et al 2000 Wilkinson & Elliman 2004, Imakita et al 2002, Ledoux et al. 2002, Yi et al. 2002.
954	1.30				
918	1.35				
886	1.40				
855	1.45				
827	1.50	1.80	SiO _x <i>a</i> -SiO ₂ silica xerogel	Si nanocluster ODC, Si nanocluster NBOHC	Cheylan et al. 2001, Sakurai 2003. Sakurai et al. 1999. Hinic et al. 1999 , Hinic et al. 2003.
800	1.55				
775	1.60				
751	1.65				
729	1.70				
708	1.75	1.85 - 1.95	silica fiber <i>a</i> -SiO ₂ & <i>α</i> -SiO ₂ SiO _x	NBOHC NBOHC NBOHC	Munekuni et al. 1990. Skuja 1992b, Cannas & Gelardi 2004. Yu et al. 2004.
689	1.80				
671	1.85				
653	1.90				
636	1.95				
620	2.00	2.0 - 2.2	<i>a</i> -SiO ₂ & silica gel ion doped <i>a</i> -SiO ₂ & <i>α</i> -SiO ₂ <i>a</i> -SiO ₂	hydrogen defects (OH, SiH or SiH ₂) H & He implantation + annealing trivalent Si center	Friebele et al. 1985, Hinic et al. 2003. Morimoto et al. 1996. Mitchell & Denure 1973, Ludwig et al.
605	2.05				
591	2.10				
577	2.15				
564	2.20				
551	2.25	2.2-2.5	<i>a</i> -SiO ₂ & <i>α</i> -SiO ₂ Ge doped <i>α</i> -SiO ₂ Si doped <i>a</i> -SiO ₂ <i>a</i> -SiO & <i>a</i> -SiO ₂ silica xerogel powder silica SiO _x	STE STE associated with Ge Si implantation + annealing Si-nanocluster organic components or <i>E'</i> center H-related defect, surface Si-H species H-related defect	Trukhin 1992, Trukhin 1993, Stevens-Kalceff 1999 Itoh et al. 1988, Luff & Townsend 1990 Kim et al. 2000c. Zacharias et al. 2003. Hinic et al. 2003. Glinka 2000, Glinka et al. 1999. Yu et al. 2004.
539	2.30				
528	2.35				
517	2.40				
506	2.45				
496	2.50				

477	2.60	Blue	2.40 - 3.00	ion doped α -SiO ₂ C doped α -SiO ₂	Sn ⁺ , Si ⁺ , Ge ⁺ , C ⁺ , Cu ⁺ implantation crystalline SiC nonoclusters	Calestani et al.2005,Perey-Rodriguez Rebohle et al. 2001a, Rebohle et al. 2002
468	2.65		2.60 - 2.80	α -SiO ₂	STE	Trukhin & Plaudis 1979,Griscom 1985
460	2.70			α -SiO ₂	STE	Hayes et al. 1984, Stevens-Kalceff 1998
451	2.75					
443	2.80					
435	2.85	Violet	2.7 - 2.75	sol-gel SiO ₂ ion doped α -SiO ₂ Si doped SiO _x	ODC, Triplet-Singlet transition of Si ODC, Si implantation neutral oxygen vacancy	Griscom 1985, Paleari 2005. Griscom 1990a, Skuja 1992a, Kuzuu Yu et al. 2004.
428	2.90		2.9 - 3.10	ion doped α -SiO ₂	O implantaition, O-related center	Hagni 1987, Chiodini et al. 2000, Ane
421	2.95			α -SiO ₂ & α -SiO ₂	O ₂ ⁻	Stevens-Kalceff 2000.
414	3.00			α -SiO ₂ , α -SiO ₂ & SiO _x	E' center	White et al. 2002.
407	3.05					
400	3.10					
394	3.15		3.10 - 3.30	α -SiO ₂	STE's associated with Ge, Al & H	Khanlary et al. 1993, Yang et al. 1994
388	3.20			ion doped α -SiO ₂ & α -SiO ₂	Al, C, & Ge implantation	Koyama 1980, Stevens-Kaceff 1998
382	3.25			α -SiO ₂	-O-O- defects	Nishikawa et al. 1992.
376	3.30			fused SiO ₂ , α -SiO ₂	O ₂ ⁻	Guzzi et al. 1987, Skuja & Trukhin 1992
370	3.50			ion doped α -SiO ₂	ODC	Anedda et al. 2003a.
365	3.40	UV	3.70	α -SiO ₂	Intrinsic defect	Alonso et al. 1983, Stevens-Kaceff & 1998
344	3.60					
342	3.65					
335	3.70			ion doped α -SiO ₂ & α -SiO ₂	Al ⁺ , H ⁺ , Li ⁺ , Na ⁺ , K ⁺ & Ge ⁺ implantation	Qin et al. 1996, Tong et al. 1997, Truk
361	3.75			α -SiO ₂	ODC or Al ³⁺ -H center	Stevens-Kalceff & Wong 2005.
295	4.20		4.20 - 4.40	α -SiO ₂ , α -SiO ₂	impurity incorporation during growth or Ge	Skuja & Trukhin 1989, Luff & Townse
292	4.25			Ge doped α -SiO ₂	oxygen vacancy related defect	Rebohle et al. 2002a, Rebohle et al. 2002b
289	4.30			α -SiO ₂	Triplet-Singlet emission of Ge	Hosono et al. 1992, Skuja 1998, Truk
285	4.35			SiO	oxygen-related defect, Si nanocluster	Yang et al 2005.
282	4.40					
279	4.45		3.70	ion doped α -SiO ₂	twofold coordinated Sn, Ge	Skuja 1992a.
276	4.50		4.20 - 4.40	sol-gel α -SiO ₂	E'-like surface center	Chiodini et al. 2000.
272	4.55			sol-gel silica	isolated silanol groups	Yao et al. 2001, Paleari et al. 2005.
270	4.60			sol-gel silica	OH-related center	Anedda et al. 2003b.
267	4.65		4.20 - 4.40	ion doped α -SiO ₂	Si excess defect	Weeks et al. 2005.
264	4.70			α -SiO ₂	ODC, Singlet-Singlet transition	Griscom 1985, Griscom 1991, Skuja
261	4.75			sol-gel α -SiO ₂	ODC, Singlet-Singlet transition of Si	Chiodini et al. 2000, Paleari et al. 2000
258	4.80			α -SiO ₂ & α -SiO ₂	divalent Ge defect	Hosono et al. 1992, Skuja 1998, Truk
				α -SiO ₂	Si implantation	Magruder et al. 2003.
				Ge doped sol-gel α -SiO ₂	GODC, Singlet-Singlet transition of Ge	Agnello et al. 2003, Trukhin et al.2003

Table 3.1 (b): Reported CL and PL luminescent bands in amorphous silicon dioxide (α -SiO₂) and crystalline quartz (α -SiO₂) and their proposed associations in Blue-UV region.

Therefore the CL spectrum is not a characteristic property of the activator but a property of the mineral. The cathodoluminescence intensity generally increases with the concentration of the activator to a maximum and then decreases. This decrease is referred to as concentration quenching (self-quenching). It can be explained by the transfer of a part of the excitation energy to other activator ions which is more effective than luminescence emission. Some ions (quenchers) show broad and intense charge transfer bands in the absorption spectrum and cause quenching of the luminescence of activators with interfering emission bands.

The quenching by ions with intense charge transfer bands especially influences the visible and the near ultraviolet (UV) spectral ranges, whereas luminescence emissions in the infrared (IR) are more or less unaffected. Apparently, the quenchers cause new closely-spaced energy levels so that the electron can easily return to the ground state with the emission of low-energy photons (IR) or by losing heat energy [Marshall, 1988].

Quenching due to lattice defects may occur if the crystal structure is damaged by mechanical processes, radiation, growth defects or impurities. These lattice defects create new energy levels between the conduction and the valence bands resulting in absorption of the excitation energy, non-luminescent energy transfer or low frequency emission. Another process which may be responsible for lowering the luminescence intensity is thermal quenching. Principally, heating of a sample results in the release of electrons and accordingly in the excitation of thermoluminescence. During irradiation of a sample with high-energy particles (e.g., electrons, ions) a part of the energy can be transformed into heat which influences the energy transfer and non-luminescent transitions. As a consequence, the luminescence intensity decreases during electron bombardment and then stabilizes.

3.4 Cathodoluminescence spectroscopy (CL)

Conventionally, there are several kinds of cathodoluminescence devices that can be installed in SEM. One of them is a spectrometer-type device, which incorporates a parabolic mirror mounted on the spectrometer port designed for high efficiency of light collection, as used in this study. This specially designed mirror is used for collecting the CL. Despite the high generation factors for the electron-hole pairs, the external photon yield is small. Furthermore, the intensity generated inside the specimen is considerably reduced by absorption in the specimen and by the total reflection at the specimen surface.

Fig. 3.5 Schematic diagram of the CL collection optics within the SEM (not to scale). The CL photons emitted by the electron-irradiated specimen are collected by a parabolic mirror and directed into the spectrograph by an optical guide.

One of the fundamental problems in CL measuring technique is therefore how to collect the emitted radiation over the largest possible solid angle with high efficiency. Fig. 3.5 shows a configuration using a parabolic mirror in which the primary electrons (PE) impact on the specimen through a hole in the parabolic mirror. Light quanta emitted into a solid angle π can be detected, where the specimen is located almost inside the mirror during the CL measurement for better CL signal collection. A silica fiber optic transmits the CL light to the entrance slit of grating spectrograph of type Spex-270M and it is registered in a single shot technique by a liquid nitrogen cooled charge coupled device CCD camera (Princeton Instruments, EEV 1024×256) with a spectral resolution of about 4 nm.

The CL was excited using a continuous stationary electron beam with energy $E_0=10$ keV and stable current of ≈ 0.6 μ A with focused beam diameter of ≈ 1 μ m in TV scanning mode both at room temperature (RT) and liquid nitrogen temperature (LNT), working distance fixed at 14 mm where the electron beam was focused on a small area ($\approx 100 \times 100$ μ m²) of the specimen surface. The CL excitation and recording use the same parameters (experimental conditions) in order to get comparable spectra collected from different silicon dioxide samples.

The visible light spectrum over the wavelengths 200-800 nm collected by the CL mirror is composed of the real luminescence light and the background light produced by the electron beam. The background spectra is registered separately and subtracted from the measured CL signal to eliminate disturbing light radiation from the thermionic cathode and other sources. The background elimination was done periodically by switching the primary electron beam on and off (beam blinking) in each start of new CL measurement.

The whole experiment was performed in high vacuum. In order to achieve a good high vacuum, some special procedures were needed. Initially, the vacuum chamber was pumped down to 10^{-2} mbar using a rotary pump. Then the chamber was pumped down to about 10^{-6} mbar using a turbomolecular pump. After 24 hours of pumping, the pressure got down to around 10^{-7} mbar and the chamber achieved the HV operation conditions, which is good enough to perform both CL and EDX measurements.

3.5 Energy dispersive X-ray spectroscopy (EDX)

X-ray spectrometry is based on the emission of X-rays from the atoms of a solid when struck by particles or waves of sufficiently high energy (electron beam in our case), followed by the relaxation of the atoms to the ground state after ionization. The X-ray spectrum produced by electron excitation consists of two parts, a continuous spectrum of deceleration radiation, known as "bremsstrahlung", and a line spectrum of the characteristic radiation. The electron beam energy is typically in the range 10-20 keV and the energy of the X-rays emitted depends on the material under examination.

X-ray data are obtained with a wavelength dispersive spectrometer. The X-ray energy dispersive system component is a semiconductor crystal which acts simultaneously as a detector and analyzer [Fuchs et al. 1990]. In a similar way as in a proportional counter tube, X-ray quanta which penetrate the semiconductor detector generate pairs of charge carriers whose number is proportional to the energy of the incident quanta. The spectrum is obtained by evaluating the pulses (current) generated and amplified in the detector system according to their height and sorting them. This takes place in a multichannel analyzer. Each channel corresponds to a specific pulse height and to a specific energy after suitable calibration. The amount of the current pulse i generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination.

The semiconductor detector is a special silicon diode called a lithium drifted silicon detector Si(Li), which is accommodated in a vacuum chamber and kept at a temperature of about 100 K by means of a cold finger. A beryllium window (about 10 μm thick) closes the evacuated chamber containing the detector and preamplifier. The window protects the detector from condensation and contamination as well as from scattered electrons and light. The entire system can be adjusted both horizontally and vertically.

Elements of low atomic number are difficult to detect by EDX. In all Si(Li) detectors, The absorption of the soft X-rays by the Beryllium window precludes the detection of elements below an atomic number of 11 (Na). In windowless systems, elements with as low atomic number as 4 (Be) have been detected, but the problems involved get progressively worse as the atomic number is reduced.

3.6 Fourier transform infrared spectroscopy (FTIR)

One of the most common methods of analyzing crystalline silica is based on the absorption of infrared light. Infrared radiation spans a part of the electromagnetic spectrum having wavelengths from 0.78 to 1000 μm . It is bounded by the red end of the visible region at high frequencies (≈ 300 THz) and the microwave region at low frequencies (≈ 300 GHz). At temperatures above absolute zero, all the atoms in molecules are in continuous vibration with respect to each other. When the frequency of a specific vibration is equal to the frequency of the IR radiation directed at the molecule, the molecule absorbs the radiation.

Fig. 3.6 Major vibrational modes for a nonlinear group, [Silverstein et al. 1981].

Different functional groups absorb characteristic frequencies of IR radiation. Thus, IR spectroscopy is an important and popular tool for structural clarification and compound identification in the sample and is even a common spectroscopic technique used for quantitative determination of compounds in mixtures. Infrared radiation is absorbed and the associated energy is converted into different types of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the middle IR region. The major types of molecular vibrations are stretching and bending. The various types of vibrations for SiO_2 are illustrated in Fig. 3.6. IR spectra are obtained by detecting changes in transmittance (T) or absorption (A) intensity as a function of frequency. Transmittance is the ratio of radiant power transmitted by the sample (I) to the radiant power incident on the sample (I_0). Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance (T), $A = \log(T^{-1}) = -\log(I/I_0)$. The transmittance spectra provide better contrast between intensities

of strong and weak bands because transmittance ranges from 0 to 100% T whereas absorbance ranges from infinity to zero.

In this study we will focus on the most frequently considered portion of the middle IR region, between 400 and 4000 cm^{-1} (25 to 2.5 μm). The total number of observed absorption bands is generally different from the total number of fundamental vibrations. It is reduced because some modes are not IR active and a single frequency can cause more than one mode of motion to occur.

Absorption bands in the region of 2500–4000 cm^{-1} usually come from stretching vibrations between hydrogen and some other atoms with a mass of 19 or less. The O–H and N–H stretching frequencies fall in the 2500–3700 cm^{-1} region, with various intensities. Hydrogen bonding has a significant influence on the peak shape and intensity, generally causing peak broadening and shifts in absorption to lower frequencies. The C–H stretching bands occur in the region of 2700–3300 cm^{-1} [Settle 1997]. The bands 2000–2300 cm^{-1} and 935–1000 cm^{-1} are associated with Si–H bond-stretching band and Si–H bond-bending type mode, respectively. Another peak at 3675 cm^{-1} corresponds to the Si–OH bond [Hosono et al. 1999].

The absorption bands at the 1850–2700 cm^{-1} region usually come only from triple bonds and other limited types of functional groups, such as $\text{C}\equiv\text{C}$ at 2100–2260 cm^{-1} , $\text{C}\equiv\text{N}$ at 2220–2260 cm^{-1} , allenes $\text{C}=\text{C}=\text{C}$ at 1900 to 2000 cm^{-1} , S–H at 2550 to 2600 cm^{-1} , P–H at 2275 to 2440 cm^{-1} [Settle 1997, Trukhin et al. 1999], Si–C at 800 cm^{-1} , Si–O at 500 cm^{-1} [Prado et al 2003].

Fig. 3.7 A single-beam IR spectrum of $\alpha\text{-SiO}_2$ and air (background), showing different Si–O vibration modes and the contribution of the ambient water and carbon dioxide CO_2 .

Moreover, the transmission spectra show peaks at 890–1062 cm^{-1} and 2260 cm^{-1} , corresponding to the Si–O stretching frequency [Tsu et al. 1989, Saito and Ikushima 2002, Suzuki et al. 2003, Prado et al 2003], at 945 cm^{-1} assigned to Si–OH mode, and at 1650 cm^{-1} associated with H–O–H (H_2O) [Gendron-Badou et al. 2003]. Typical FTIR spectra in the range 400–4000 cm^{-1} of air and pure $\alpha\text{-SiO}_2$ layer are shown in Fig. 3.7, where some vibrational modes of Si–O and hydrogen incorporated molecules are pointed. Commonly

the transmission peaks at 1100, 471 cm^{-1} are attributed respectively to triply degenerated stretching and bending vibration modes of the tetrahedron, but 800 cm^{-1} corresponds to an inter-tetrahedral Si–O–Si bending vibration mode [Gendron-Badou et al. 2003].

Most commercial instruments to separate and measure IR radiation use dispersive spectrometers or Fourier transform spectrometers. Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. An IR spectrometer consists of three basic components: radiation source, interferometer (monochromator in dispersive IR system), and detector. Infrared transmittance measurements were performed using a FTIR spectrometer (Nicolet Magna IR 550) in the spectral range 400–4000 cm^{-1} . The spectral resolution was fixed to 4 cm^{-1} and the spectra were recorded at room temperature (RT) by means of non-polarized light under normal incidence. Most benchtop FTIR spectrometers are single-beam instruments. Unlike double-beam grating spectrometers, single-beam FTIR does not obtain transmittance or absorbance IR spectra in real time. A typical operating procedure is described as follows: A background spectrum (Fig. 3.7) is first obtained by collecting an interferogram (raw data), followed by processing the data by Fourier transform conversion. This is a response curve of the spectrometer and takes account of the combined performance of source, interferometer, and detector. The background spectrum (air) also includes the contribution from any ambient water (two irregular groups of lines at about 3600 cm^{-1} and about 1600 cm^{-1}) and carbon dioxide (doublet at 2360 cm^{-1} and sharp spike at 667 cm^{-1} present in the optical bench. Next, a single-beam sample spectrum is collected, it contains absorption bands from the sample and the background (air). The background spectra have been eliminated in order to get the real vibrational response of the sample. Reference samples of the silicon substrate have also been used for background division.

4. References

- Agnello S. , Boscaino R. , Buscarino, Cannas M. and Gelardi F. M. : *Structural relaxation of E' centers in amorphous silica*, Phys. Rev. B 66 (2002) 113201.
- Agnello S. , Boscaino R. , Cannas M. , Cannizzo A. , Gelardi F. M., Grandi S. and Leone M. : *Temperature and excitation energy dependence of decay processes of luminescence in Ge-doped silica*, Phys. Rev. B 68 (2003) 165201.
- Alonso P. J., Halliburton L. E. , Kohnke E. E. and Bossoli R .B. : *X-ray-induced luminescence in crystalline SiO₂*, J. Appl. Phys. 54 (1983) 5369.
- Anedda A. , Carbonaro C. M. , Clemente F. and Corpino R. : *Ultraviolet excitation fine tuning of luminescence bands of oxygen-deficient centers in silica*, J. Appl. Phys. 92 (2002) 3034.
- Anedda A. , Carbonaro C. M. , Clemente F. , Corpino R , Corpino R. and Serpi A. : *Excitation pattern of the blue emission in Ge-doped silica*, J. Non-Cryst. Solids 315 (2003a) 161.
- Anedda A. , Carbonaro C. M. , Clemente F. , Corpino R. , Grandi S. , Mustarelli P. and Magistris A. : *OH-dependence of ultraviolet emission in porous silica*, J. Non-Cryst. Solids 322 (2003b) 68.
- Arnold G. W. : *Ion-implantation effects in noncrystalline SiO₂*, IEEE Trans. Nucl. Sci. NS 20 (1973) 220.
- Awazu K. and Kawazoe H.: *O₂ molecules dissolved in synthetic silica glasses and their photochemical reactions induced by ArF excimer laser radiation*, J. Appl. Phys. 68 (1990) 3584.

- Bakos T. , Rashkeev S. N. and Pantelides S. T. : *H₂O and O₂ molecules in amorphous SiO₂: Defect formation and annihilation mechanism* , Phys. Rev. B 69 (2004a) 195206.
- Bakos T. , Rashkeev S. N. and Pantelides S. T.: *Optically active defects in SiO₂: The nonbridging oxygen center and interstitial OH molecule*, Phys. Rev. B 70 (2004b) 75203.
- Barfels T. : PhD dissertation , *Kathodolumineszenz amorpher und kristalliner Modifikationen von SiO₂ und GeO₂*, Rostock university (2001).
- Baulch D. L. , Cox R. A. , Hampton R. F. , Kerr J. A. , Troe J. and Watson R. T.: *Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, CODATA Task Group on Chemical Kinetics*, J. Phys. Chem. Ref. Data 9 (1980) 295.
- Bell R. J. and Dean P. : *The Structure of Vitreous Silica: Validity of the Random Network Theory*, Philosophical Magazine 25 (1972) 1381.
- Berry F. J. and Vaughan D. J. (eds) : *Chemical bonding and spectroscopy in mineral chemistry*, Chapman and Hall, London, (1985).
- Bobyshev A. A. and Radtsig V. A. : *Optical absorption spectra of paramagnetic defects in vitreous silica* , Sov. Phys. Chem. Glass 14 (1988) 501.
- Boero M. , Pasquarello A. , Sarnthein. and Car R. : *Structure and Hyperfine Parameters of E'₁ Centers in alpha-Quartz and in Vitreous SiO₂*, Phys. Rev. Lett. 78 (1997) 887.
- Boscaino R. , Cannas M. , Gelardi F. M. and Leone M. : *Photoluminescence band at 4.4 eV in oxygen-deficient silica: temperature effects*, J. Phys.: Condens. Matter 8 (1996) L545.
- Bosio C. and Czaja W. : *The fundamental absorption edge of crystalline and amorphous SiO₂*, Europhys. Lett. 24 (1993) 197.
- Brunner G. O. , Wondratschek H. and Laves F. : *Ultrarotuntersuchung über den Einbau von H in natürlichen Quartz*, Z. Electrochem 56 (1961) 735.
- Calestani D. , Lazzarini L. , Salvati G. and Zha M. : *Morphological, structural and optical study of quasi-1D SnO₂ nanowires and nanobelts*, Cryst. Res. Technol. 40 (2005) 937.
- Cannas M. , Agnello S. , Boscaino R. , Gelardi F. M. , Leone M. and Boizot B. : *Optical properties of oxygen-deficiency related centers in amorphous SiO₂ investigated by synchrotron*, Radiation effects and Defects in Solids 157 (2002) 1045.
- Cannas M. , Agnello S. , Boscaino R. , Gelardi F. M. , Grandi S. and Mustarelli P. C.: *Ultraviolet emission lifetime in Si and Ge oxygen deficient centers in silica*, J. Non-Cryst. Solids 322 (2003) 129.
- Cannas M. and Gelardi F. M. : *Vacuum ultraviolet excitation of the 1.9 eV emission band related to nonbridging oxygen hole centers in silica*, Phys. Rev. B 69 (2004) 153201.
- Cannizzo A. , Agnello S. , Grandi S. , Leone M. , Magistris A. and Radzig V. A.: *Luminescence activity of surface and interior Ge-oxygen deficient centers in silica*, J. Non-Cryst. Solids 351 (2005) 1805.
- Cartier E. , Stathis J. H. , and Buchanan D. A. : *Passivation and depassivation of silicon dangling bonds at the Si/SiO₂ interface by atomic hydrogen* , Appl. Phys. Lett. (1993) 1510.
- Carvalho W. , Dumas P. , Corset J. and Neuman V. : *Raman Spectra and Oxygen-Related Absorption Bands in Pure Silica Core Fibres*, J. Raman Spectrosc. 16 (1985) 330.
- Chae K. H. , Son J.H., Chang G. S. , Kim H. B. , Jeong J. Y. , Im S. , Song J. H., Kim K. J., Kim H. K. and Whang C. N. : *Visible photoluminescence in ion beam mixed SiO₂/Si/SiO₂ layers*, NanoStructured Materials 11 (1999) 1239.
- Cheyman S. , Elliman R. G. , Gaff K. , Durand A. : *Luminescence from Si nanocrystals in silica deposited by helicon activated reactive evaporation*, Appl. Phys. Lett. 78 (2001) 1670.

- Chiodini N. , Meinardi F. , Morazzoni F. , Paleari A. , Scotti R. and Martino D. Di. : *Ultraviolet photoluminescence of porous silica*, Appl. Phys. Lett. 76 (2000) 3209.
- Edwards A. H. , Fowler W. B. and Robertson J. : *Structure and imperfections in amorphous and crystalline silicon dioxide* , R. Devine A. B. , Duraud J.-P. and Dooryhe E. (eds.), John Wiley & Sons Ltd., (2000), p.253.
- Fair R. B. : *Physical models of boron diffusion in ultrathin gate oxides*, J. Electrochem. Soc. 144 (1997) 708.
- Fan X. D. , Peng J. L. and Bursill L. A. : *Joint Density of States of Wide-Band-Gap Materials by Electron Energy Loss Spectroscopy*, Modern Phys. Lett. B 12 (1998) 541.
- Fanderlik I. (ed.) : *Silica Glass and its Application* , Glass Science and Technology 11, ELSEVIER, Amsterdam, (1991).
- Feigl F. J. , Fowler W. B. and Yip K. L. : Oxygen vacancy model for the E' center in SiO₂, Solid State Commun. 14 (1974) 225.
- Feder R. , Spiller E. and Topalian J. : *X-Ray Lithography*, Polymer Eng. Sci. 17 (1977) 385.
- Finlayson -Pitts B. J. and Pitts J. N. : Jr., *Atmospheric Chemistry, Fundamental sand Experimental Techniques*, John Wiley, New York, (1986).
- Fitting H.-J. , Ziems T. , von Czarnowski A. and Schmidt B. : *Luminescence center transformation in wet and dry SiO₂*, Radiation Measurements 39 (2004) 649.
- Friebele E. J. , Griscom D. L. , Stapelbroek M. and Weeks R. A. : *Fundamental Defect Centers in Glass: The Peroxy Radical in Irradiated, High-Purity, Fused Silica*, Phys. Rev. Lett. 42 (1979) 1346.
- Friebele E. J. , Griscom D. L. and Marrone M. J. : The optical absorption and luminescence bands near 2 eV in irradiated and drawn synthetic silica} , J. Non-Cryst. Solids 71 (1985) 133.
- Fuchs E. , Oppolzer H. and Rehme H. : *Particle Beam Microanalysis: Fundamental, Methods and Applications*, VCH Verlagsgesellschaft, Weinheim, (1990).
- Gerber Th. and Himmel B. : *The Structure of Silica Glass*, J. Non-Cryst. Solids 83 (1986) 324.
- Gendron-Badou A. , Coradin T. , Maquet J. , Frhlich F. and Livage J. : *Spectroscopic characterization of biogenic silica*, J. Non-Cryst. Solids 316 (2003) 331.
- Glinka Y. D. , Lin S.-H. and Chen Y.-T. : *The photoluminescence from hydrogen-related species in composites of SiO₂ nanoparticles*, Appl. Phys. Lett. 75 (1999) 778.
- Glinka Y. D. : *Two-photon-excited luminescence and defect formation in SiO₂ nanoparticles induced by 6.4-eV ArF laser light*, Phys. Rev. B 62 (2000) 4733.
- Gobsch G. , Haberlandt H. , Weckner H.-J. and Reinhold J. : phys. stat. sol. (b) 90 (1978) 309.
- Gorton N. T. , Walker G. , Burley, S. D. : *Experimental analysis of the composite blue CL emission in quartz - is this related to aluminium content?* In: Abstracts SLMS International Conference on Cathodoluminescence, Nancy, Sept (1996) , p.59.
- Griggs D. T. and Blacic J. D. : Quartz : Anomalous weakness of synthetic crystals, Science 147 (1965) 292.
- Griggs D. T. : *Hydrolytic weakening of quartz and other silicates*, Geophys. J. R. Astron. Soc. 14 (1967) 19.
- Griscom D. L. , Friebele E. J. and Sigel G. H. : *Observation and analysis of the primary ²⁹Si hyperfine structure of the E' center in non-crystalline SiO₂* , Solid State Commun. 15 (1974) 479.
- Griscom D. L. : *The electronic structure of SiO₂: A review of recent spectroscopic and theoretical advances*, J. Non-Cryst. Solids 24 (1977) 155.

- Griscom D. L. : *E' center in glassy SiO₂ : Microwave saturation properties and confirmation of the primary ²⁹Si hyperfine structure*, Phys. Rev. B 20 (1979a) 1823.
- Griscom D. L. : Proc. 33rd Frequency Control Symposium (Electronic Industrial Association, Washington, DC, (1979b), p.98.
- Griscom D. L. : *E' center in glassy SiO₂: ¹⁷O, ¹H, and "very weak" ²⁹Si superhyperfine structure*, Phys. Rev. B 22 (1980) 4192.
- Griscom D. L. , Stapelbroek M. and Friebele E. J. : *ESR studies of damage processes in X-irradiated high purity α-SiO₂:OH and characterization of the formyl radical defect*, J. Chem. Phys. 78 (1983) 1638.
- Griscom D. L. : *Characterization of three E'-center variants in X- and γ-irradiated high purity α-SiO₂*, Nucl. Instrum. and Methods Phys. Res. B 1 (1984) 481.
- Griscom D. L. : *Defect structure of glasses : Some outstanding questions in regard to vitreous silica*, J. Non-Cryst. Solids 73 (1985) 51.
- Griscom D. L. and Friebele E. J. : *Fundamental radiation-induced defect centers in synthetic fused silicas: Atomic chlorine, delocalized E' centers, and a triplet state*, Phys. Rev. B 34 (1986) 7524.
- Griscom D. L. : *Glass Science and Technology*, D. R. Uhlmann and N. J. Kreidl (eds), Academic, London, Vol. 4B (1990a) 151.
- Griscom D. L. : *Optical Properties and Structure of Defects in Silica Glass*, J. of the Ceramic Society of Japan 99 (1991) 899.
- Griscom D. L. : *The natures of point defects in amorphous silicon dioxide*, Pacchioni et al. (eds.) , *Defects in SiO₂ and related Dielectrics: Science and Technology*, Kluwer Academic Publishers, (2000), p.117.
- Guzzi M. , Martini M. , Mattaini M. , Pio F. and Spenolo G. : *Luminescence of fused silica: Observation of the O₂⁻ emission band*, Phys. Rev. B 35 (1987) 9407.
- Hagni R. D. : *Industrial applications of cathodoluminescence microscopy*. In: Hagni R. D. (ed.): *Process Mineralogy IV: Applications to precious metal deposits, industrial minerals, coal, liberation, mineral processing, agglomeration, metallurgical products, and refractories, with special emphasis on cathodoluminescence microscopy*. TMS, Warrendale, Pennsylvania, (1987), p.37.
- Hayes W. , Kane M. J. , Salminen O. , Wood R. L. and Doherty S. P. : *ODMR of recombination centres in crystalline quartz*, J. Phys. C 17 (1984) 2943.
- Hayes W. and Jenkin T. J. L. : *Paramagnetic hole centres produced in germanium-doped crystalline quartz by X-irradiation at 4K*, J. Phys. C 18 (1985) L849.
- Hayes W. and Stoneham A. M. : *Defects and Defect Processes in Nonmetallic Solids*, John Wiley, New York, (1985).
- Hayes W. and Jenkin T. J. L. : *Optically detected magnetic resonance studies of exciton trapping by germanium in quartz*, J. Phys. C 21 (1988) 2391.
- Heggie M. I. : *A molecular water pump in quartz dislocations*, Nature 355/23 (1992) 337.
- Henderson G. S. and Baker D. R. (eds.) : *Synchrotron Radiation: Earth, Environmental and Material Sciences Applications*, Short Course Series 30, Mineralogical Association of Canada. (2002)159-178. Henderson G. S. , *The Geochemical News*, number 113, October (2002), pp.13.
- Hinic I. , Stanisic G. and Popovic Z. : *Photoluminescence properties of silica aerogel during sintering process*, J. Sol-Gel Science and Technology 14 (1999) 281.

- Hinic I. , Stanisic G. and Popovic Z. : *Influence of the synthesis conditions on the photoluminescence of silica gels*, J. Serb. Chem. Soc. 68 (2003) 953.
- Hosono H. , Abe Y. , Imagawa H. , Imai H. and Arai K. : *Experimental evidence for the Si-Si bond model of the 7.6-eV band in SiO₂ glass*, Phys. Rev. B 44 (1991) 12043.
- Hosono H. , Abe Y. , Kinser D. L. , Weeks R. A. , Muta K. and Kawazoe H. : *Nature and origin of the 5-eV band in SiO₂:GeO₂ glasses*, Phys. Rev. B 46 (1992) 11445.
- Hosono H. , Mizuguchi M. , Kawazoe H. and Ogawa T. : *Effects of fluorine dimer excimer laser radiation on the optical transmission and defect formation of various types of synthetic SiO₂ glasses*, Appl. Phys. Lett. (1999) 2755.
- Im S. , Jeong J. Y. , Oh M. S. , Kim H. B. , Chae K. H. , Whang C. N. and Song J. H. : *Enhancing defect-related photoluminescence by hot implantation into SiO₂ layers*, Appl. Phys. Lett. 47 (1999) 961.
- Imai H. , Arai K. , Saito T. , Ichimura S. Nonaka H. , Vigroux J. P. , Imagawa H. , Hosono H. and Abe Y. : *UV and VUV optical absorption due to intrinsic and laser induced defects in synthetic silica glasses*, in R. A. B. Devine (ed.), *The physics and Technology of Amorphous SiO₂*, Plenum, New York, (1987), p.153.
- Imai H. , Arai K. , Imagawa H. , Hosono H. and Abe Y. : *Two types of oxygen-deficient centers in synthetic silica glass*, Phys. Rev. B 38 (1988) 12772.
- Imakita K. , Fujii M. , Yamaguchi Y. , and Hayashi S. : *Interaction between Er ions and shallow impurities in Si nanocrystals within SiO₂*, Phys. Rev. B 71 (2005) 115440.
- Isoya J. , Weil J. A. and Halliburton L. E. : *EPR and ab initio SCF-MO studies of the Si-H – Si system in the E'₄ center of α -quartz*, J. Chem. Phys. 74 (1981) 5436.
- Itoh C. , Tanimura K. and Itoh N. : *Optical studies of self-trapped excitons in SiO₂*, J. Phys. C : Solid State Phys. 21 (1988) 4693.
- Itoh C. , Tanimura K. , Itoh N. and Itoh M. : *Threshold energy for photogeneration of self-trapped excitons in SiO₂*, Phys. Rev. B 39 (1989) 11183.
- Itoh C. , Suzuki T. and Itoh N. : *Luminescence and defect formation in undensified and densified amorphous SiO₂*, Phys. Rev. B 41 (1990) 3794.
- Kajihara K., Skuja L., Hirano M. and Hosono H.: *Formation and decay of the nonbridging oxygen hole centers in SiO₂ glasses induced by F₂ laser irradiation: In situ observation using a pump and probe technique*, Appl. Phys. Lett. 79 (2001) 1757.
- Kajihara K. , Ikuta Y. , Hirano M. and Hosono H. : *Effect of F₂ laser power on defect formation in high-purity SiO₂ glass*, J. Non-Cryst. Solids 322 (2003) 73.
- Kajihara K. , Skuja L. , Hirano M. and Hosono H. : *Role of Mobile Interstitial Oxygen Atoms in Defect Processes in Oxides: Interconversion between Oxygen-Associated Defects in SiO₂ Glass*, Phys. Rev. Lett. 92 (2004) 15504.
- Kanemitsu Y. , Suzuki K. , Kondo M. and Matsumoto H. : *Luminescence from a cubic silicon cluster*, Solid State Commun. 89 (1994) 619.
- Khanlary M. R. , Townsend P. D. and Townsend J. E. : *Luminescence spectra of germanosilicate optical fibres.1: radioluminescence and cathodoluminescence*, J. Phys. D 26 (1993) 371.
- Khriachtchev L. , Räsänen M. , Novikov S. and Pavesi L. : *Systematic correlation between Raman spectra, photoluminescence intensity, and absorption coefficient of silica layers containing Si nanocrystals*, Appl. Phys. Lett. 85 (2004) 1511.
- Kim H. B. , Son J. H. , Whang C. N. , Chae K. H. , Lee W. S. , Im S. , Kim S. O. , Woo J. J. and Song J. H. : *Light-Emitting Properties of Si-Ion-Irradiated SiO₂/Si/SiO₂ Layers*, J. the Korean Phys. Soci. 37 (2000a) 466.

- Kim H. B. , Son J. H. , Chae K. H. , Jeong J. Y. , Lee W. S. , Im S. , Song J. H. and Whang C. N. : *Photoluminescence from Si ion irradiated SiO₂ Si SiO₂ films with elevated substrate temperature*, Materials Science and Engineering B 69-70 (2000b) 401.
- Kim H. B. , Kim T. G. , Son J. H. , Whang C. N. , Chae K. H. , Lee W. S. , Im S. and Song J. H. , *Effects of Si-dose on defect-related photoluminescence in Si-implanted SiO₂ layers*, J. Appl. Phys. 88 (2000c) 1851.
- Kofstad P. : *High Temperature Corrosion*, ELSEVIER, London and New York, (1988).
- Koyama H. : *Cathodoluminescence study of SiO₂*, J. Appl. Phys. 51 (1980) 2228.
- Krbetschek M. R. , Götze J. , Dietrich A. and Trautmann T. : *Spectral Information from Minerals Relevant for Luminescence Dating*, Radiation Measurements 27 (1997) 695.
- Kronenberg A. K. , Kirby S.H. , Aines R. D. and Rossmann G. R. : *Solubility and diffusional uptake of hydrogen in quartz at high water pressure: implications for hydrolytic weakening in the laboratory and within the earth*, Tectonophysics 172 (1986) 255.
- Kuzuu N. and Murahara M. : *X-ray-induced absorption bands in type-III fused silicas*, Phys. Rev. B 46 (1992) 14486.
- Lamkin M. , Riley F. and Fordham R. : *Oxygen Mobility in Silicon Dioxide and Silicate Glasses: A Review*, J. Eur. Ceram. Soc. 10 (1992) 347.
- Lau H. W. , Tan O. K. , Liu Y. , Ng C. Y. , Chen T. P. , Pita K. and Lu D. : *Defect-induced photoluminescence from tetraethylorthosilicate thin films containing mechanically milled silicon nanocrystals*, J. Appl. Phys. 97 (2005) 104307.
- Ledoux G. , Gong J. , Huisken F. , Guillois O. and Reynaud C. : *Photoluminescence of size-separated silicon nanocrystals: Confirmation of quantum confinement*, Appl. Phys. Lett. 80 (2002) 4834.
- Lee W. S. , Jeong J. Y. , Kim H. B. , Chae K. H. , Whang C. N. , Im S. and Song J. H. : *Violet and orange luminescence from Ge-implanted SiO₂ layers*, Materials Science and Engineering B 69-70 (2000) 474.
- Lide D. R. : *CRC Handbook of Chemistry and Physics*, 85th edition, CRC Press, (2004).
- Lu Z. Y. , Nicklaw C. J. , Fleetwood D. M. , Schrimpf R. D. and Pantelides S. T. : *Structure, Properties, and Dynamics of Oxygen Vacancies in Amorphous SiO₂*, Phys. Rev. Lett. 89 (2002) 285505.
- Ludwig M. H. , Menniger J. , Hummel R. E. : *Cathodoluminescing properties of spark-processed silicon*, J. Phys: Condens. Matter 7 (1995) 9081
- Luff B. J. and Townsend P. D. : *Cathodoluminescence of synthetic quartz*, J. Phys. Condensed Matter 2 (1990) 8089.
- Magruder R. H. , Weeks R. A. and Weller R. A. : *Luminescence and absorption in type III silica implanted with multi-energy Si, O and Ar. ions*, J. Non-Cryst. Solids 322 (2003) 58.
- Majid F. B. and Miyagawa I. : *Detection of Several Types of E'-center by ESR Double Modulation Spectrum Method*, Chem. Phys. Lett. 209 (1993) 496.
- Marshall D. J. : *Cathodoluminescence of geological materials*, Allen & Unwin Inc., Winchester Mass., (1988).
- McLaren A. C. , Cook R. F. , Hyde S. T. , Tobin R. C. : *The mechanisms of the formation and growth of water bubbles and associated dislocation loops in synthetic quartz*, Phys. Chem. Minerals 9 (1983) 79.
- Mitchell J. P. and Denure D. G. : *A study of SiO layers on Si using cathodoluminescence spectra*, Solid State Electron. 16 (1973) 825.

- Mohanty T. , Mishra N. C. , Bhat S. V. , Basu P. K. and Kanjilal D. : *Dense electronic excitation induced defects in fused silica*, J. Phys. D: Appl. Phys. 36 (2003) 3151.
- Morimoto Y. , Igarashi T. , Sugahara H. and Nasu S. : *Analysis of gas release from vitreous silica*, J. Non-Cryst. Solids 139 (1992) 35.
- Morimoto Y. , Weeks R. A. , Barnes A. V. , Tolk N. H. and Zuhr R. A. : *The effect of ion implantation on luminescence of a silica*, J. Non-Cryst. Solids 196 (1996) 106.
- Mozzi R. L. and Warren B. E. : *The Structure of Vitreous Silica*, J. Appl. Crystallogr. 2 (1969) 164.
- Munekuni S. , Yamanaka T. , Shimogaichi Y. , Tohmon R. , Ohki Y. , Nagasawa K. and Hama Y. : *Various types of nonbridging oxygen hole center in high-purity silica glass*, J. Appl. Phys. 68 (1990) 1212.
- Mysovsky A. S. , Sushko P. V. , Mukhopadhyay S. , Edwards A. H. and Shluger A. L.: *Calibration of embedded-cluster method for defect studies in amorphous silica*, Phys. Rev. B 69 (2004) 85202.
- Nicholas J. B. , Hopfinger A. J. , Trouw F. R. and Iton E. : *Molecular Modeling of Zeolite Structure. 2. Structure and Dynamics of Silica Sodalite and Silicate Force Field*, J. Am. Chem. Soc. 113 (1991) 4792.
- Nicollian E. H. and Brews J. R. : *MOS (Metal Oxide Semiconductor) Physics and Technology*, WILEY-VCK, New York, (2002).
- Nishikawa H. , Shiroyama Y. , Nakamura R. , Ohki Y. , Nagasawa K. and Hama Y.: *Photoluminescence from defect centers in high-purity silica glasses observed under 7.9-eV excitation*, Phys. Rev. B 45 (1992) 586.
- Nishikawa H. , Watanabe E. , Ito D. and Ohki Y. : *Decay kinetics of the 4.4 eV photoluminescence associated with the two states of oxygen-deficient-type defect in amorphous SiO₂*, Phys. Rev. Lett. 72 (1994) 2101.
- Nishikawa H. : *Structure and properties of amorphous silicon dioxide-Isuse on the reliability and novel applications*, Chapter 3 pp.93 in: Hari Singh Nalwa, Silicon-Based Materials and Devices, Vol. 2, (2001).
- Nuttall R. H. D. and Weil J. A. : *Two hydrogenic trapped-hole species in α -quartz*, Solid State Commun. 33 (1980) 99.
- O'Reilly E. P. and Robertson J. : *Theory of defects in vitreous silicon dioxide*, Phys. Rev. B 27 (1983) 3780.
- Ozawa L. : *Cathodoluminescence: Theory and Application* , Kodansha Ltd., Japan, (1990).
- Pacchioni G. and Ierano G. : *Optical Absorption and Nonradiative Decay Mechanism of E' Center in Silica*, Phys. Rev. Lett. 81 (1998a) 377.
- Pacchioni G. and Ierano G. : *Ab initio theory of optical transitions of point defects in SiO₂*, Phys. Rev. B 57 (1998b) 818.
- Pacchioni G. , Skuja L. and Griscom D. L. : *Defects in SiO₂ and related dielectrics: Science and technology*, (2000), p.73.
- Paleari A. , Chiodini N. , Di Martino D. and Meinardi F. : *Radiative decay of vacuum-ultraviolet excitation of silica synthesized by molecular precursors of Si-Si sites: An indicator of intracenter relaxation of neutral oxygen vacancies*, Phys. Rev. B 71 (2005) 75101.
- Pellergrino P. , Perez-Rodriguez A. , Garrido B. , Gonzalez-Varona O. , Morante J. R., Marcinkevicius S. , Galeckas A. and Linnros J. : *Time-resolved analysis of the white photoluminescence from SiO₂ films after Si and C coimplantation*, Appl. Phys. Lett. 84 (2004) 25.

- Perez-Rodriguez A. , Gonzalez-Varona O. , Garrido B. , Pellegrino P. , Morante J. R., Bonafos C. , Carrada M. and Claverie A. : *White luminescence from Si⁺ and C⁺ ion-implanted SiO₂ films*, J. Appl. Phys. 94 (2003) 254.
- Plaksin O. A. , Takeda Y. , Okubo N. , Amekura H. , Kono K. , Umeda N. , Kishimoto N. : *Electronic transitions in silica glass during heavy-ion implantation*, Thin Solid Films 464-465 (2004) 264.
- Prado R. J. , D'Addio T. F. , Fantini M. C. A. , Pereyra I. and Flank A. M. : *Annealing effects of highly homogeneous a-Si_{1-x}C_x:H*, J. Non-Cryst. Solids 330 (2003) 196.
- Qin G. G. , Lin J. , Duan J. Q. and Yao G. Q. : *A comparative study of ultraviolet emission with peak wavelengths around 350 nm from oxidized porous silicon and that from SiO₂ powder*, Appl. Phys. Lett. 69 (1996) 1689.
- Rafferty C. S. : *Stress Effects in Silicon Oxidation Simulation and Experiments*, PhD thesis , Stanford University, (1989).
- Rebohle L. , Gebel T. , Fröb H. , Reuther H. and Skorupa W. : *Ion beam processing for Si/C-rich thermally grown SiO₂*, Appl. Surf. Sci. 184 (2001a) 156.
- Rebohle L. , Gebel T. , von Borany J. , Skorupa W. , Helm M. , Pacifici D. , Franzo G. and Priolo F. : *Transient behavior of the strong violet electroluminescence of Ge-implanted SiO₂ layers*, Appl. Phys. B 74 (2002a) 53.
- Rebohle L. , von Borany J. , Fröb H. , Gebel T. , Helm M. and Skorupa W. : *Ion beam synthesized nanoclusters for silicon-based light emission*, Nucl. Instrum. Methods Phys. Res. B 188 (2002b) 28.
- Reimer L. : *Scanning Electron Microscopy: Physics of Image Formation and Microanalysis*, Springer series in optical sciences, Vol. 45, (1998).
- Robertson J. : *The Physics and Technology of Amorphous SiO₂*, Roderich A. B. Devine (ed.), National center for Telecommunication Studies, Meyland, France, (1988).
- Rudra J. K. , Fowler B. W. and Feigl F. J. : *Model for the E'₂ center in Alpha Quartz* , Phys. Rev. Lett. 55 (1985) 2614.
- Saito K. and Ikushima A. J. : *Effects of fluorine on structure, structural relaxation, and absorption edge in silica glass*, J. Appl. Phys. 91 (2002) 4886.
- Sakurai Y. , Nagasawa K. , Nishikawa H. and Ohki Y. : *Characteristic red photoluminescence band in oxygen-deficient silica glass*, J. Appl. Phys. 86 (1999) 370.
- Sakurai Y. : *Oxygen-related red photoluminescence bands in silica glasses*, J. Non-Cryst. Solids 316 (2003) 389.
- Seol K. S. , Ohki Y. , Nishikawa H. , Takiyama M. and Hama Y. : *Effect of implanted ion species on the decay kinetics of 2.7 eV photoluminescence in thermal SiO₂ films*, J. Appl. Phys. 80 (1996) 6444.
- Settle F. A. (ed.) : *Handbook of Instrumental Techniques for Analytical Chemistry*, Prentice Hall, (1997).
- Shimizu-Iwayama T. , Ohshima M. , Niimi T. , Nakao S. , Saitoh K. , Fujita T. and Itoh N. : *Visible photoluminescence related to Si precipitates in Si⁺-implanted SiO₂*, J. Phys.: Condens. Matter 5 (1993) L375.
- Shimizu-Iwayama T. , Nakao S. and Saitoh K. : *Optical and structural characterization of implanted nanocrystalline semiconductors*, Nucl. Instrum. Methods Phys. Res. B 121 (1997) 450.
- Skuja L. , Streletsky A. N. and Pakovich A. B. : *A new intrinsic defect in amorphous SiO₂: Twofold coordinated silicon*, Solid State Commun. 50 (1984) 1069.

- Skuja L. and Trukhin A. : Comment on " Luminescence of fused silica: Observation of the O_2^- emission band, Phys. Rev. B 39 (1989) 3909.
- Skuja L. : Isoelectronic series of twofold coordinated Si, Ge, and Sn atoms in glassy SiO_2 : a luminescence study, J. Non-Cryst. Solids 149 (1992a) 77.
- Skuja L. : Time-resolved low temperature luminescence of non-bridging oxygen hole centers in silica glass, Solid State Commun. 84 (1992b) 613.
- Skuja L. : The origin of the 1.9eV luminescence band in glassy SiO_2 , J. Non-Cryst. Solids 179 (1994a) 51.
- Skuja L. , Suzuki T. , Tanimura K. : Site-selective laser-spectroscopy studied of the intrinsic 1.9-eV luminescence center in glassy SiO_2 , Phys. Rev. B 52 (1995) 15208.
- Skuja L. : Optically active oxygen-deficiency-related centers in amorphous silicon dioxide, J. Non-Cryst. Solids 239 (1998) 16.
- Skuja L. , Güttler B. , Schiel D. and Silin A. R. : Quantitative analysis of the concentration of interstitial O_2 molecules in SiO_2 glass using luminescence and Raman spectroscopy, J. Appl. Phys. 83 (1998a) 6106.
- Skuja L. , Güttler B. , Schiel D. and Silin A. R. : Infrared photoluminescence of preexisting or irradiation-induced interstitial oxygen molecules in glassy SiO_2 and α -quartz, Phys. Rev B 58 (1998b) 14296.
- Skuja L. , Optical properties of defects in silica, pp.73-116 in Pacchioni G., Skuja L. and Griscom D. L. (eds) : Defects in SiO_2 and related dielectrics: Science and technology, (2000).
- Skuja L. , Hirano M. and Hosono H. : Oxygen-Related Intrinsic Defects in Glassy SiO_2 : Interstitial Ozone Molecules, Phys. Rev. Lett. 84 (2000a) 302.
- Skuja L. , Mizuguchi M. , Hosono H. and Kawazone H. : The nature of the 4.8 eV optical absorption band induced by vacuum-ultraviolet irradiation of glassy SiO_2 , Nucl. Instrum. Methods Phys. Res. B 166-167 (2000b) 711.
- Skuja L. , Kajihara K. , Kinoshita T. , Hirano M., Hosono H. : The behavior of interstitial oxygen atoms induced by F_2 laser irradiation of oxygen-rich glassy SiO_2 , Nucl. Instr. & Methods in Physics Research B 191 (2002) 127.
- Skuja L. , Kajihara K. , Hirano M. , Saitoh A. , Hosono H. : An increased F_2 -laser damage in 'wet' silica glass due to atomic hydrogen: A new hydrogen-related E' -center, J. Non-Cryst. Solids 352 (2006) 2297.
- Slater J. C. : Quantum Theory of Molecules and Solids: Symmetry and Energy Bands in Crystals, McGraw-Hill, New York, Vol. 2, (1965).
- Snyder K. C. and Fowler W. B. : Oxygen vacancy in α -quartz: A possible bi- and metastable defect, Phys Rev. B 48 (1993) 13238.
- Song J. , Corrales L. R. , Kresse G. and Jonsson H. : Migration of O vacancies in alpha-quartz: The effect of excitons and electron holes, Phys. Rev. B 64 (2001) 134102.
- Song K. S. and Williams R. T. : Self-Trapped Excitons, Springer Verlag, Berlin, (1993).
- Stapelbroek M. , Griscom D. L. , Friebele E. J. and Sigel Jr. G. H. : Oxygen-associated trapped-hole centers in high-purity fused silicas, J. Non-Cryst. Solids 32 (1979) 313.
- Stevens-Kalceff M. A. and Philips M. R. : Cathodoluminescence microcharacterization of the defect structure of quartz, Phys. Rev. B 52 (1995) 3122.
- Stevens-Kalceff M. A. : Cathodoluminescence microcharacterization of the defect structure of irradiated hydrated and anhydrous fused silicon dioxide, Phys. Rev. B 57 (1998) 5674.
- Stevens-Kalceff M. A. : Electron-Irradiation-Induced Radiolytic Oxygen Generation and Microsegregation in Silicon Dioxide Polymorphs, Phys. Rev. Lett. 84 (2000) 3137.

- Stevens-Kalceff M. A. , Stesmans A. and Wong J. : *Defects induced in fused silica by high fluence ultraviolet laser pulses at 355 nm*, Appl. Phys. Lett. 80 (2002) 758.
- Stevens-Kalceff M. A. and Wong J. : *Distribution of defects induced in fused silica by ultraviolet laser pulses before and after treatment with a CO₂ laser*, J. Appl. Phys. 97 (2005) 113519.
- Streletsky A. N. , Pakovich A. B. , Gachkovski V. F. , Aristov Yu. I. , Rufov Yu. N. and Butyagin P. Y. : *Khim. Fizika*, Sov. Chem. Phys., No.7 (1982) 938.
- Suzuki T. , Skuja L. , Kajihara K. , Hirano M. , Kamiya T. and Hosono H. : *Electronic Structure of Oxygen Dangling Bond in Glassy SiO₂: The Role of Hyperconjugation*, Phys. Rev. Lett. 90 (2003) 186404.
- Takagahara T. and Takeda K. : *Theory of the quantum confinement effect on excitons in quantum dots of indirect-gap materials*, Phys. Rev. B 46 (1992) 15578.
- Tanimura K. , Tanaka T. and Itoh N. : *Creation of Quasistable Lattice Defects by Electronic Excitation in SiO₂*, Phys. Rev. Lett. 51 (1983) 423.
- Tong S. , Liu X.-N. , Gao T. and Bao X.-M. : *Intense violet-blue photoluminescence in as-deposited amorphous Si:H:O films*, Appl. Phys. Lett. 71 (1997) 698.
- Trukhin A. N. : *Investigation of the Photoelectric and Photoluminescent Properties of Crystalline Quartz and Vitreous Silica in the Fundamental Absorption Region*, phys. stat. sol. (b) 86 (1978) 67.
- Trukhin A. N. and Plaudis A. E. : *Investigation of intrinsic luminescence of SiO₂* , Sov. Phys. Solid State 21 (1979) 644.
- Trukhin A. N. : *Study of Exitons in SiO₂- Luminescent Centers as Exciton Detectors*, phys. stat. sol. (b) 98 (1980) 541.
- Trukhin A. N. : *Excitons in SiO₂: a review*, J. Non-Cryst. Solids 149 (1992) 32.
- Trukhin A. N. : *Luminescence of a self-trapped exciton in GeO₂ crystal*, Solid State Commun. 85 (1993) 723.
- Trukhin A. N. : *Self-trapped exciton luminescence in α -quartz*, Nucl. Instr. and Meth. in Phys. Res. B 91 (1994) 334.
- Trukhin A. N. , Goldberg M. , Jansons J. , Fitting H.-J. and Tale I. A. : *Silicon dioxide thin film luminescence in comparison with bulk silica*, J. Non-Cryst. Solids 223 (1998) 114.
- Trukhin A. N. and Fitting H.-J. : *Investigation of optical and radiation properties of oxygen deficient silica glasses*, J. Non-Cryst. Solids 248 (1999) 49.
- Trukhin A. N. , Jansons J. , Fitting H.-J. , Barfels T. and Schmidt B. : *Cathodoluminescence decay kinetics in Ge⁺, Si⁺, O⁺ implanted SiO₂ layers*, J. Non-Cryst. Solids 331 (2003a) 91.
- Trukhin A. , Poumellec B. and Garapon J. : *Study of the germanium luminescence in silica: from non-controlled impurity to germano-silicate core of telecommunication fiber performs* , J. Non-Cryst. Solids 332 (2003b) 153.
- Trukhin A. and Poumellec B. : *Photosensitivity of silica glass with germanium studied by photoinduced of thermally stimulated luminescence with vacuum ultraviolet radiation*, J. Non-Cryst. Solids 324 (2003c) 21.
- Tsu D. V. , Lucovsky G. and Davidson B. N. : *Effects of the nearest neighbors and the alloy matrix on SiH stretching vibrations in the amorphous SiO_r:H (0<r<2) alloy system*, Phys. Rev. B 40 (1989) 1795.
- Uchino T. , Takahashi M. and Yoko T. : *Model of oxygen-deficiency-related defects in SiO₂ glass*, Phys. Rev. B 62 (2000b) 2983.
- Uchino T. , Takahashi M. and Yoko T. : *Structure and Generation Mechanism of the Peroxy-Radical Defect in Amorphous Silica*, Phys. Rev. Lett. 86 (2001) 4560.

- van Santen R. A. , de Man A. J. M. , Jacobs W. P. J. H. , Teunissen E. H. and Kramer G. J. : *Lattice Relaxation of Zeolites*, Catalysis Letters 9 (1991) 273.
- Weeks R. A. : *Paramagnetic Resonance of Lattice Defects in Irradiated Quartz*, J. Appl. Phys. 27 (1956) 1376.
- Weeks R. A. and Nelson C. M. : *Trapped electrons in irradiated quartz and silica. I. Optical absorption*, J. Am. Ceram. Soc. 43 (1960) 399.
- Weeks R. A. : *Paramagnetic Spectra of E' Centers in Crystalline Quartz*, Phys. Rev. 130 (1963) 570.
- Weeks R. A. , Magruder R.H. , Gaylon R. and Weller R.A. : *Effects of B and N implantation on optical absorption and photoluminescence and comparison to the effects of implanting Si, Ge, O, and Ar in silica*, J. Non-Cryst. Solids 351 (2005) 1727.
- Weber J. T. and Cromer D. T. : *Orbital Radii of Atoms and Ions*, J. Chem. Phys. 42 (1965) 4116.
- Wilkinson A. R. and Elliman R. G. : *The effect of annealing environment on the luminescence of silicon nanocrystals in silica*, J. Appl. Phys. 96 (2004) 4018.
- White B. D. , Brillson L. J. , Bataiev M. , Brillson L. J. , Fleetwood D. M. , Schrimpf R. D. , Choi B. K. , Fleetwood D. M. and Pantelides S. T. : *Detection of trap activation by ionizing radiation in SiO₂ by spatially localized cathodoluminescence spectroscopy*, J. Appl. Phys. 92 (2002) 5729.
- Yacobi B. G. and Holt D. B. : *Cathodoluminescence Microscopy of Inorganic Solids*, Plenum Press, New York and London, (1990).
- Yang X. H. , Townsend P. D. and Holgate S. A. : *Cathodoluminescence and depth profiles of tin in float glass* , J. Phys. D 27 (1994) 1757.
- Yang X. , X. , Wua L. , Li S. H. , Li H. , Qiu T. , Yang Y. M. , Chu P. K. and Siu G. G. : *Origin of the 370-nm luminescence in Si oxide nanostructures* , Appl. Phys. Lett. 86 (2005) 201906.
- Yao B. , Shi H. , Zhang X. and Zhang L. : *Ultraviolet photoluminescence from nonbridging oxygen hole centers in porous silica*, Appl. Phys. Lett. 78 (2001) 174.
- Yi L. X. , Heitmann J. , Scholz R. and Zacharias M. : *Si rings, Si clusters, and Si nanocrystals-different states of ultrathin SiO_x layers*, Appl. Phys. Lett. 81 (2002) 4248.
- Yi L. X. , Heitmann J. , Scholz R. and Zacharias M. : *Phase separation of thin SiO layers in amorphous SiO/SiO₂ superlattice during annealing*, J. Phys. : Condens. Matter 15 (2003) S2887.
- Yip K. L. and Fowler W. B. : *Electronic structure of E'₁ centers in SiO₂* , Phys. Rev. B 11 (1975) 2327.
- Yu Z. , Aceves M. , Carrillo J. , Flores F. , Falcony C. , Domínguez C. , Llobera A. and Morales-Acevedo A. : *Photoluminescence in off-stoichiometric silicon oxide compounds*, Superficies y Vacío 17 (2004) 1.
- Zacharias M. , Tsybeskov L. , Hirschman K. D. , Fauchet P. M. , Bläsing J. , Kohlert P. and Veit P. : *Nanocrystalline silicon superlattices: fabrication and characterization*, J. Non-Cryst. Solids 227-230 (1998) 1132.
- Zacharias M. , Heitmann J. , Scholz R. , Kahler U. , Schmidt M. and Bläsing J. : *Size-controlled highly luminescent silicon nanocrystals: A SiO/SiO₂ superlattice approach*, Appl. Phys. Lett. 80 (2002) 661.
- Zacharias M. , Yi L. X. , Heitmann J. , Scholz R. , Reiche M. and Gösele U. : *Size-controlled Si nanocrystals for photonic and electronic applications*, Solis State Phenomena 94 (2003) 95.
- Zatsepin A. F. , Biryukov D. Yu. and Kortov V. S. : *Analysis of OSEE Spectra of Irradiated Dielectrics*, Latvian Journal of Physics and Technical Sciences. No.6 (2000) 83.
- Zhang B. L. and Raghavachari K. : *Photoabsorption and photoluminescence of divalent defects in silicate and germanosilicate glasses: First-principles calculations*, Phys. Rev. B 55 (1997), 15993.
- Zunger A. and Wang L.-W. : *Theory of silicon nanostructures* , Appl. Surf. Sci. 102 (1996) 350.

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The exciting world of crystalline silicon is the source of the spectacular advancement of discrete electronic devices and solar cells. The exploitation of ever changing properties of crystalline silicon with dimensional transformation may indicate more innovative silicon based technologies in near future. For example, the discovery of nanocrystalline silicon has largely overcome the obstacles of using silicon as optoelectronic material. The further research and development is necessary to find out the treasures hidden within this material. The book presents different forms of silicon material, their preparation and properties. The modern techniques to study the surface and interface defect states, dislocations, and so on, in different crystalline forms have been highlighted in this book. This book presents basic and applied aspects of different crystalline forms of silicon in wide range of information from materials to devices.

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